

EVALUATION OF POINT AND BROAD SOURCES OF CHEMICAL AND BIOLOGICAL
IMPAIRMENT OF THE NINE MILE RUN WATERSHED

by

Jason Brooks Willis

B.S. in Plastics Engineering Technology, Pennsylvania State University, 2007

Submitted to the Graduate Faculty of
Swanson School of Engineering in partial fulfillment
of the requirements for the degree of
M.S. in Civil and Environmental Engineering

University of Pittsburgh

2011

UNIVERSITY OF PITTSBURGH
SWANSON SCHOOL OF ENGINEERING

This thesis was presented

by

Jason Brooks Willis

It was defended on

June 28, 2011

and approved by

Ronald D. Neufeld, Ph.D., Professor, Department of Civil and Environmental Engineering

Willie F. Harper, Jr., Ph.D., Associate Professor, Department of Civil and Environmental Engineering

Daniel Bain, Ph.D., Assistant Professor, Department of Geology and Planetary Science

Thesis Advisor: Jason D. Monnell, Ph.D., Research Assistant Professor, Department of Civil and
Environmental Engineering

Copyright © by Jason Brooks Willis

2011

EVALUATION OF POINT AND BROAD SOURCES OF CHEMICAL AND BIOLOGICAL IMPAIRMENT OF THE NINE MILE RUN WATERSHED

Jason Brooks Willis, M.S.

University of Pittsburgh, 2011

This thesis evaluates the water quality within the Nine Mile Run Watershed of Allegheny County, PA. Due to its large land area and proximity to several city neighborhoods, the water originating in Frick Park is significantly impacted by people, dogs, and vehicles. These inputs can lead to water quality degradation of its receiving body Nine Mile Run (NMR), as well as its tributaries Falls Ravine Creek (FR) and Fern Hollow Creek (FH). NMR eventually flows into the Monongahela River across from Homestead. While the overall contribution to flow volume on the Monongahela River is small, studying the water quality of the Nine Mile Run Watershed can serve as an example for other tributaries and local rivers in similar settings. Study results could provide data and evidence for future grants, further infrastructure improvement, and improvement to the health and drinking water quality of Pittsburgh and waters downstream on the Ohio River.

To accomplish a characterization of water quality and identification of sources of impairment, bimonthly samples were taken from September 2010 through May 2011 at 11 locations along Nine Mile Run and its tributaries. Sampling sites were strategically located to analyze contamination from three main sources including, a combined sewer overflow (CSO)

outfall, Hot Dog Dam, and traffic from Forbes Avenue and I-376. During each sampling period, field and lab measurements were conducted for each sample site.

In comparison to its Frick Park tributaries, NMR displayed higher pH, TDS, and bacterial counts throughout the study. Sodium and chloride concentrations were also higher in NMR during colder months due to deicing agent application on adjacent roadways. The CSO had an effect on the upstream and downstream sites of NMR by yielding lower DO and pH values throughout the study. NMR sites and the CSO also produced the highest Enterococci counts during the study, while Site 12 had the single highest E. Coli count. Data suggests that the water quality in the Nine Mile Run Watershed was adversely affected throughout the study by deicing agents, pet and human waste, and input from combined and sanitary sewers.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	xv
1.0 INTRODUCTION/BACKGROUND	1
1.1 TECHNICAL SITE DESCRIPTIONS.....	7
1.1.1 Site 1 – Combined Sewer Overflow (CSO) Outfall.....	7
1.1.2 Site 2 – Downstream from Commercial Avenue	9
1.1.3 Site 3 – Upstream of CSO Outfall	10
1.1.4 Site 4 – NMR Bend Next to Park Bench	11
1.1.5 Site 5 – Adjacent to Walking Bridge on NMR	12
1.1.6 Site 6 – Fern Hollow Park Bridge Crossing.....	14
1.1.7 Site 7 – Falls Ravine Creek.....	15
1.1.8 Site 8 – Fern Hollow Beneath Forbes Avenue Bridge.....	17
1.1.9 Site 9 – Drainage Pool Adjacent to Tranquil Trail	18
1.1.10 Site 10 – Tranquil and Homewood Trail Intersection on Fern Hollow	19
1.1.11 Site 12 – Downstream of Hot Dog Dam on Fern Hollow.....	20
2.0 STATEMENT OF THE PROBLEM	22
2.1 POSSIBLE CONTAMINANTS.....	25
2.1.1 Deicing Agents.....	25

2.1.2	Combined Sewer Overflows (CSO) and Sanitary Sewer Overflows (SSO).....	27
2.1.3	Fecal Contamination	29
3.0	METHODS AND INSTRUMENTATION	31
3.1	FIELD MEASUREMENTS	31
3.2	LAB MEASUREMENTS	32
3.2.1	Turbidity	32
3.2.2	Total Dissolved Solids (TDS).....	34
3.2.3	Measuring Bacteria Plates.....	37
3.2.4	Determination of Enterococci Bacteria by Membrane Filtration	41
3.2.5	Determination of Escherichia Coli (E. Coli) by Membrane Filtration	43
3.2.6	Atomic Absorption Spectrometry	46
3.2.7	Chloride Combination Ion Selective Electrode (ISE).....	50
3.2.8	Ion Chromatograph (IC)	51
4.0	RESULTS AND DISCUSSION	55
4.1	COMBINED SEWER OVERFLOW INFLUENCE.....	55
4.1.1	The Affect of CSO on pH	55
4.1.2	Dissolved Oxygen Concentration in Frick Park Streams and the CSO	59
4.2	METAL CONCENTRATIONS	62
4.2.1	Sodium	63
4.2.2	Divalent Cations.....	67
4.2.2.1	Calcium	67
4.2.2.2	Magnesium.....	69
4.2.3	Potassium	71

4.3	MAJOR ANIONS (NO_3^- , SO_4^{2-} , Cl^-)	73
4.3.1	Chloride.....	73
4.3.2	Nitrate	76
4.3.3	Sulfate	80
4.3.4	Charge Balance	82
4.4	BACTERIAL CONTAMINATION.....	85
4.4.1	Enterococci	85
4.4.2	E. Coli	88
4.4.3	Turbidity	89
5.0	SUMMARY AND CONCLUSIONS	92
5.1	RECOMMENDATIONS	96
6.0	BIBLIOGRAPHY	98

LIST OF TABLES

Table 3-1: Formula for 250mL of Plate Count Agar at pH 7.0+/- 0.2.....	39
Table 3-2: Components for 150mL of m-Azide Agar	42
Table 3-3: Components for 100mL of m TEC Agar Used for E. Coli Samples.....	44
Table 3-4: IC Operating Conditions For the Dionex 4500i Ion Chromatograph.....	52
Table 4-1: Site Specific Sodium Concentration Values and % Differences for 2/4/2011 and 3/10/2011. Table shows 2.5 – 14x increases in sodium concentration especially between sites 6 and 9 that reside within wooded areas of the Park.	66
Table 4-2: Charge Balance for Cations and Anions during various conditions during sampling. Concentrations were evaluated during Spring and Winter conditions. A percent difference was calculated between the positively and negatively charges parameters for each date on NMR sites (2-5).	84

LIST OF FIGURES

Figure 1-1: Frick Park and Surrounding Area With Denoted Sampling Sites.....	3
Figure 1-2: Site 1 - Combined Sewer Overflow Outfall on NMR.....	8
Figure 1-3: Site 2 – Pool Across Commercial Avenue on NMR.....	9
Figure 1-4: Site 3 – Upstream from CSO Outfall on NMR.....	11
Figure 1-5: Site 4 – At Bend and Bench on NMR down from Braddock Trail intersection	12
Figure 1-6: Site 5 - Adjacent to Wooden Walking Bridge on NMR	13
Figure 1-7: Site 6 - Outflow From Under Park Road Bridge on Fern Hollow	14
Figure 1-8: Site 7 – Downstream of Dilapidated Bridge on Falls Ravine	16
Figure 1-9: Site 8 – Below Forbes Bridge and Upstream of Hot Dog Dam on Fern Hollow.....	17
Figure 1-10: Site 9 – Drainage Pool That Flows Into Fern Hollow.....	18
Figure 1-11: Site 10 – Outflow of Homewood Trail Bridge on Fern Hollow	20
Figure 1-12: Site 12 – Upstream of Biddle Trail Bridge on Fern Hollow	21
Figure 2-1: Contamination at Combined Sewer Overflow Site.....	24
Figure 2-2: Source of Contamination in Hot Dog Dam on Fern Hollow	24
Figure 3-1: Hach 2100 A Turbidimeter and Standards 0.61-1000 NTU	33
Figure 3-2: Gooch Crucibles After Filtration and Drying Showing Various Concentrations of TSS.....	37
Figure 3-3: Heterotrophic Bacteria Plate Post-Incubation.....	40

Figure 3-4: Enterococci Plated Samples Post-Incubation Showing NMR Sites on the Left and Sites 8 and 7 on the Right	43
Figure 3-5: Coli Plated Samples Post Incubation Showing E. Coli Negative (Left) and Positive (Right) Samples	45
Figure 3-6: Perkin Elmer Model 1100B Atomic Absorption Spectrophotometer Used to Find Concentration Values of Cationic Species.....	47
Figure 3-7: Potassium Cathode Lamp in the Perkin Elmer Model 1100B Plugged Into HCL1 and Port 1	48
Figure 3-8: 0.45µm Filters After Filtering 100mL of Sample. Darker Color Caused by High Concentrations of Suspended Sediment.....	49
Figure 3-9: Dionex 4500i Ion Chromatograph	51
Figure 3-10: Sample Chloride Calibration Curve. Similar Curves Were Used to Determine the Concentration of Chloride, Nitrate, and Sulfate in All Samples.....	53
Figure 4-1: Field Measurements of pH at site 1 (CSO), site 2 (downstream of CSO), and site 3 (upstream of CSO) on NMR. The CSO consistently had a lower pH than other NMR sites throughout the study.	57
Figure 4-2: Average pH for in NMR, Fern Hollow, and Falls Ravine for each month of the study. Falls ravine had the lowest average pH of the study, while NMR consistently had the highest values between 7.5 and 8.4.....	58
Figure 4-3: DO values for Site 1 (CSO), Site 2 (downstream), and Site 3 (upstream) of NMR displaying the low DO characteristics present at the CSO outfall.....	60

Figure 4-4: Dissolved Oxygen Concentrations in NMR, Fern Hollow, and Falls Ravine Over Entire Sampling Period (9/10 – 5/11). NMR averaged the highest DO concentrations throughout the study, with high points occurring during winter months.....	62
Figure 4-5: Sodium Concentration for in NMR, Fern Hollow, and Falls Ravine throughout the study. NMR exceeds other tributaries during every sampling period causing potential impairment to downstream biota.	64
Figure 4-6: Sodium Concentrations (mg/L) During a High Snowfall Period (2/4/11) and a High Rainfall Event (3/10/11). Sodium concentrations are 3-4 times higher in NMR because of road salt during high snowfall periods.	65
Figure 4-7: Monthly Calcium Concentrations From 9/20/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. Fern Hollow had highest calcium concentrations throughout the study, with peaks occurring during the winter months.....	69
Figure 4-8: Monthly Magnesium Concentrations From 9/20/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. Fern Hollow produced the highest average Magnesium concentrations throughout the study. Seasonal patterns did not follow deicing agent usage, but rather showed higher concentrations during warmer months.	70
Figure 4-9: Monthly Potassium Concentrations From 12/3/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. Fern Hollow consistently yielded the highest potassium concentrations throughout the study.	72
Figure 4-10: Monthly Chloride Concentrations From 12/3/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. High snowfall periods 1/7/11 and 2/4/11 yielded the highest chloride concentrations of the sampling period.	74

Figure 4-11: Frick Park Stream Chloride Concentrations Over Duration of 12/3/2010 – 5/16/2011. NMR possessed the highest chloride concentrations throughout the study, especially in the winter months.....	76
Figure 4-12: Nitrate Concentrations for Each Sampling Site from 12/3/10 – 5/16/11. Sampling on 1/7/11 yielded the highest values of Nitrate, which were 4.2 times higher than the next highest values during 5/9/11.	78
Figure 4-13: Nitrate Concentrations for Each Site without data from the 1/7/11 sampling period. The warmer months of April and May 2011 when fertilizers are typically applied had the highest nitrate concentrations.	79
Figure 4-14: Sulfate Concentrations at each site for a sampling period of 12/3/10 – 5/16/11. The highest sulfate concentrations occurred during the 5/9/11 sampling.....	80
Figure 4-15: Sulfate Concentrations in NMR, Fern Hollow, and Falls Ravine between 12/3/10 – 5/16/11. Fern Hollow averaged the highest sulfate concentrations over the sampling period, but Falls Ravine had the single highest value of 417 mg/L.....	82
Figure 4-16: Enterococci Plate Counts at for the CSO, NMR, Site 7, Fern Hollow Sites, and Site 12. CSO and NMR had the highest number of CFU/100mL throughout the study, while site 12 consistently yielded higher colony numbers than Fern Hollow sites.....	86
Figure 4-17: Fern Hollow vs. Site 12 Enterococci Concentrations at Six Sampling Dates (12/3/10 – 5/16/11). Site 12 had higher concentrations of enterococci at 5/6 sampling dates.....	87
Figure 4-18: E. Coli Plate Counts for 5 Sampling Dates (1/7/11 – 5/16/11) at the CSO site 1, NMR sites, Site 7, Fern Hollow Sites, and Site 12. Site 12 had the single highest count of the sampling period, while NMR averaged the highest.....	89

Figure 4-19: Monthly Turbidity (NTU) from 9/20/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. NMR yielded the highest turbidity readings of the study during the high flow event on 3/10/11.....	91
--	----

ACKNOWLEDGMENTS

Most of all, I would like to sincerely thank my advisor, Dr. Jason D. Monnell, for providing countless hours of his time and effort into this research project. His guidance and knowledge helped tremendously throughout the project, especially in the initial and final phases. His knack for humor was always well received during times of stress and hardship. Dr. Monnell has also expanded my knowledge and helped steer me toward my goals and interests pertaining to laboratory and fieldwork.

I would like to thank my M.S. committee members: Dr. Ronald Neufeld, Dr. Willie Harper, Jr., and Dr. Dan Bain for participating in my defense, and providing me with valuable input. I enjoyed the classes that I have had with them, and I feel that the knowledge I have gained will fully prepare me for a professional career in environmental engineering.

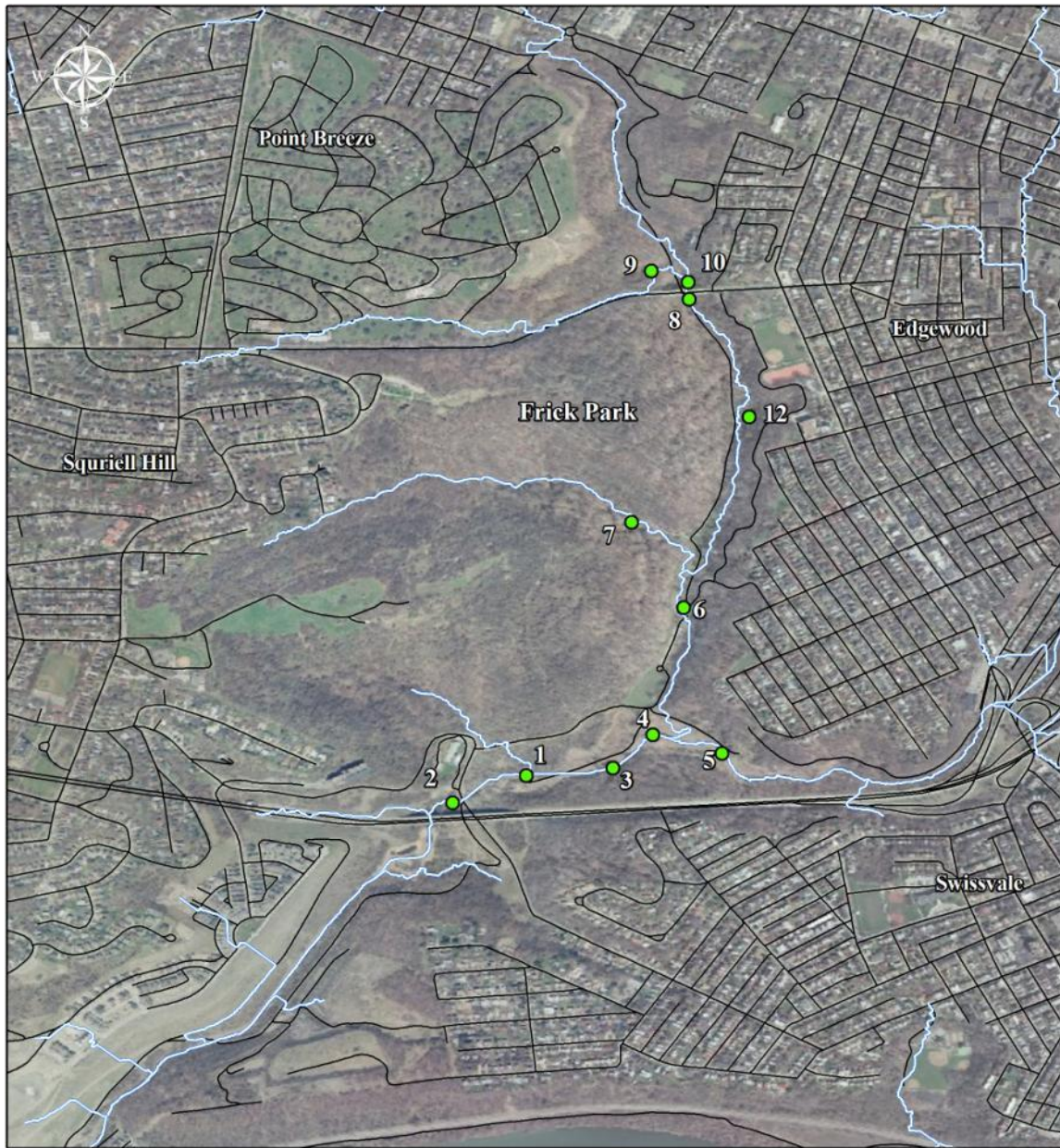
I would also like to thank my mother and father for always providing me with support and advice over this long academic journey. It would not have been possible without their encouragement and love along the way. My girlfriend and friends have also provided unconditional support and advice along the way that have helped me achieve this accomplishment.

1.0 INTRODUCTION/BACKGROUND

With such heavy pedestrian usage within Frick Park, it is imperative to monitor the water quality and distinguish causes of harmful impacts so they can be mitigated before further damage is done. For example, direct contributions to NMR from sewer systems need to stop before restoration can take place. Human health and sustainability are of the utmost importance in Frick Park since it has numerous facilities for recreational and cultural use. With large events throughout the year such as Kinder Camps, the Great Race, sports leagues, and picnics, maintaining the Park, its ecosystem, and watershed are necessary for public health. This study investigated the water quality of Nine Mile Watershed, which is made up of the Nine Mile Run, Fern Hollow and Falls Ravine streams. Although substantial stream portions are buried within Frick Park, only the aboveground sections of the aforementioned streams were studied. This was done to gather a better understanding of the conditions that exist in the Nine Mile Run Watershed, and provide data and evidence for future grants and infrastructure improvements within Frick Park.

Sampling areas were located in the City of Pittsburgh's largest regional park, 561-acre Frick Park. It is the youngest Pittsburgh Park and has been open since 1927. **Figure 1-1** represents the study area of Frick Park, which is bordered on the northern side by the Point Breeze neighborhood, Squirrel Hill neighborhood on the western border, Edgewood on the eastern border, and Swissvale on the southern border. Frick Park partially contains the Nine

Mile Run Watershed. The path of Nine Mile Run (NMR) is shown in **Figure 1-1** on the lower portion of the map between Edgewood and Swissvale. Sampling points 1-5 are located on NMR, while sites 6-12 are on tributary streams within Frick Park. NMR is underground in a concrete culvert upstream and east of Frick Park. During this underground stretch, NMR receives a large flow input from several culverted branches that contribute flow in the form of storm sewers from Wilkinsburg, Pittsburgh, and Edgewood (Collins *et al.*, 1998). The main branch of NMR is the Wilkinsburg Culvert that passes through Wilkinsburg and Edgewood. Two additional storm sewers contribute year-round flow adjacent to the mouth of the Wilkinsburg Culvert from beneath I-376 and Edgewood Towne Center (Collins *et al.*, 1998). NMR emerges from a culvert under South Braddock Avenue in Swissvale, and travels west along the I-376 Parkway. From the culvert, NMR flows overland for 1.8 miles until it reaches a confluence with the Monongahela River across from the town of Homestead.



Legend

- Streams
- Roads/Access Roads

Coordinate System: NAD83

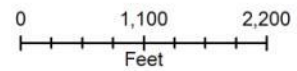


Figure 1-1: Frick Park and Surrounding Area With Denoted Sampling Sites

Various types of landscapes were present in the park including flat plains, steep valleys, urbanized pavement, and wooded slopes. Frick Park is also marked by drastic changes in topography from the valley floors to the steep hillsides. The steep terrain, combined with the impermeable surfaces of surrounding neighborhoods, promotes high runoff rates and flash flooding during large precipitation events. Being located between Regent Square, Point Breeze, Homewood, Swissvale, and Squirrel Hill neighborhoods, in addition to having very little development within, Frick Park is a hot spot for outdoor enthusiasts. It is very popular among hikers, bikers, animal watchers, and it is quite pet friendly with two off-leash dog parks and a Hot Dog Dam water play area on Fern Hollow Creek. Due to its heavy population density and proximity to the interstate, the surrounding area also sees large amounts of automotive traffic from various roads that pass around or through the park. Commercial Avenue, Forbes Avenue, South Braddock Avenue, and the I-376 highway are the most traveled routes that have potential to influence the park. The United States Army Corp of Engineers (USACOE) and the City of Pittsburgh has completed extensive ecological restoration work in Frick Park, and organizations such as Nine Mile Run Watershed Association work to maintain the environmental and aesthetic quality. In addition to serving as an outdoor recreational location for the public, the Frick Park Environmental Center and Environmental Charter School provide environmental education to people of all ages through demonstrations using the Park's natural resources. It is this direct public interaction with the Watershed that makes it important to evaluate the water quality for potential sources of contamination.

The bedrock in the Nine Mile Run Watershed consists of horizontal layers of shale, sandstone, claystone, limestone, and coal (Collins *et al.*, 1998). Over the past 10,000 years, NMR cut and eroded its valley from 280.1 meters to the present level of the Monongahela River,

which is 219.5 meters (Collins *et al.*, 1998). Nine Mile Run Creek drains an area of 19.4 km² and is located in a highly dissected portion of the unglaciated Appalachian Plateau Physiographic Province, with a total relief in the drainage basin of 180m (Koryak *et al.*, 2001a). Fern Hollow possesses a total drainage area of 4.9 km² and can be classified into an upper and lower section (Koryak *et al.*, 2001a). The upper Fern Hollow section is primarily urbanized and is influenced by runoff from the Pittsburgh boroughs of Homewood, Point Breeze, and Wilkinsburg. Runoff from Forbes Avenue, Braddock Avenue, and several other side streets flows into the upper section of Fern Hollow. The upper section of Fern Hollow transitions from an urbanized landscape to parkland at the Biddle Trail entrance. The lower section of Fern Hollow passes through fields, wetlands, and wooded areas before flowing into NMR at the intersection of the Nine Mile Run and Braddock Trails. Lower Fern Hollow has a larger “buffer” of trees, shrubs, and other vegetation than the upper section, which is more directly influenced by the drainage of paved surfaces. The Falls Ravine section is entirely wooded for its duration, with no road runoff contributions, and a small number of houses by its headwaters. Falls Ravine Creek flows from west to east until its confluence with Fern Hollow. As opposed to Fern Hollow and NMR, Falls Ravine Creek is spring-fed and its headwaters start by the bottom portion of Forest Glen Road, which is located in the Squirrel Hill neighborhood. Falls Ravine flows through a steep valley and parallels the Falls Ravine walking trail for most of the duration. During the winter of 2009-10, numerous trees and branches fell, as well as large amounts of erosion that caused a lot of damage to the stream channel, bridges, and adjacent walking trail. All of this damage required stream restoration, bridge rebuilding, and a slight re-route of the trail during the summer of 2010.

This investigation included sample collection at 11 predetermined sites along Nine Mile Run, Fern Hollow, and Falls Ravine. Water samples were taken bi-monthly at each site,

targeting different flows, and seasonal conditions between September 2010 – May 2011. At each sample site, measurements of dissolved oxygen (DO), pH, total dissolved solids (TDS), and temperature (°C) will be measured in the field. In addition to these parameters, laboratory procedures will be conducted to determine existence and concentration of selected cations (calcium, magnesium, sodium, and potassium), anions (sulfate, chloride, phosphate, and nitrate), *Escherichia Coli* (E. Coli), Enterococci, TDS, total suspended solids (TSS), and turbidity (NTU).

The sample locations were selected to pinpoint potential and suspected sources of contamination that included deicing agents, CSO influence, and fecal matter. Site locations are presented in **Figure 1-1**. Sites 1-5 are all in the southern portion of Frick Park on Nine Mile Run bordering the I-376 highway. The focus of these sites was to evaluate the contributions of automobile byproducts, road deposits (construction materials and deicing agents), CSOs, and sanitary sewers to various contaminant concentration levels. Site 2 is directly below the I-376 Bridge and downstream from the CSO outlet at site 1. Site 3 is 200 yards upstream from the CSO, while sites 4 and 5 are respectively upstream from 3. Sites 6 -12 track north along the eastern boarder of the park and the Edgewood neighborhood. Site 6 is under the Fern Hollow Bridge crossing on one of the park roads, and site 7 is up the Falls Ravine Trail next to a dilapidated bridge that is downstream from a recent trail remediation site. Moving north up Tranquil Trail, site 12 was selected before a stone bridge crossing on the Biddle Trail. To obtain data regarding potential fecal contamination, site 12 was used because it is downstream from the Hot Dog Dam. Site 8 lies underneath the Forbes Bridge and is upstream of the Hot Dog Dam. The location of site 8 and will provide a comparison to site 12. Upstream, sites 9 and 10 are diagonally across the Tranquil trail from each other. Site 9 is located in a sewer-drainage pool on the west side of Tranquil Trail while site 10 is located underneath a stone bridge crossing at

the intersection of the Homewood and Tranquil Trail. Site 11 was dried up at the time of sampling and is at the very northern part of the park between the Homewood and Hawthorne trails. It is in the run-off section of a ravine and lost its source when most of the surrounding trees were removed to prevent the spread of Oak-Wilt Disease. Further in-depth site descriptions will be discussed later in the paper.

It is the objective of this study to produce useful information that would be available to adjacent communities about the water quality in Frick Park. This data would help inform residents of any existing water quality issues, which might affect children or young adults that play in the streams. The resultant data will be beneficial to organizations such as, the Parks Conservancy, Nine Mile Run Watershed Association, and the City of Pittsburgh. These organizations could use the data to help develop remediation techniques, future grants, and infrastructure improvements that would help maintain the environmental quality of Frick Park.

1.1 TECHNICAL SITE DESCRIPTIONS

1.1.1 Site 1 – Combined Sewer Overflow (CSO) Outfall

Sampling site 1 is at the outfall of the CSO shown in **Figure 1-2**. This site was selected to observe the influence of a CSO system on NMR, and the upstream and downstream sites. The CSO is one possible source of oxygen deficient water and fecal contamination, so this site provided a good comparison with other NMR stream sites. This CSO is a box culvert that runs underground along Fern Hollow, and is fed by several diversion chambers (Collins *et al.*, 1998). After crossing beneath the Braddock Trail, the CSO runs underneath a visible concrete viaduct

driveway for about 400 yards before emptying into Nine Mile Run just upstream from the Commercial Avenue crossing. Both banks of the sampling site are filled with rock while some vegetation exists on the left bank.



Figure 1-2: Site 1 - Combined Sewer Overflow Outfall on NMR

Water had a tendency to pool up at the CSO outfall due to lack of current during low flows, allowing for accumulation of leaves, other organic matter, dead animals, and garbage. Flow from the CSO is highly dependent on rainfall and NMR flow velocity. This site usually emitted a foul odor due to decaying matter, as well as dead rodents and accumulated trash.

1.1.2 Site 2 – Downstream from Commercial Avenue

Site 2 is shown in **Figure 1-3** and lies about 0.2 miles downstream of site 1, directly adjacent to the I-376 Bridge with respect to NMR flow, and before the Squirrel Hill Tunnel. Just above this site, NMR is diverted beneath Commercial Avenue by a large concrete pipe. This site was the deepest of all 11 sampling sites due to the steep banks that existed on both sides of the stream.



Figure 1-3: Site 2 – Pool Across Commercial Avenue on NMR

This site was selected because it is directly to the side of Commercial Avenue, and it is the closest site to a heavily traveled road. Commercial Avenue crossed no more than 3 meters upstream of this site, leaving a high potential for vehicle and road contamination. The location of site 2 was also significant in regards to deicing agents and fecal contamination, due to the proximity of the I-376 Bridge, as well as being directly downstream of the CSO site. As stated

earlier, water at site 2 is approximately 1 meter deep and flow is usually slow with some eddy currents. Watercolor is also usually medium opacity green with large amounts of silt covering rocks and streambed. Asphalt, rocks, concrete blocks, and old concrete made up the majority of both banks and bottom structure.

1.1.3 Site 3 – Upstream of CSO Outfall

This site was selected because it is upstream of site 1, the CSO, which provided insight into the water quality above and below the CSO. **Figure 1-4** depicts sampling site 3. The flow is always shallow, quite accelerated, and the fastest of all sites. It is located before a bend in the stream that straightens into the confluence of the CSO outflow. Watercolor is dependent on degree of flow, but is usually crystal-clear. Both sides of the bank are rocky in the streambed but have ample vegetation in the form of shrubs, small trees and grass. This site helped quantify the impact of the CSO because it is first site upstream.



Figure 1-4: Site 3 – Upstream from CSO Outfall on NMR

1.1.4 Site 4 – NMR Bend Next to Park Bench

Sample site 4 is several hundred yards upstream from site 3, and is shown in **Figure 1-5**. It is in front of a park bench and occurs on a bend in the stream immediately upstream of a makeshift rock dam, so flow is calm and slow. Due to the slow flow and deeper conditions created by the rock dam, high quantities of leaves and other debris agglomerate on the streambed of this site. The selection of this site was based on the large amounts of foot traffic, observations of dogs, and contributions of highway runoff and sewage. Pets have frequently been observed swimming and frolicking in the deeper section of this site, upstream of the rocks in the right side of **Figure 1-5**. The left bank, in the foreground of **Figure 1-5**, is on a walking trail with a bench and sees a lot of pet, walker, and biker traffic.



Figure 1-5: Site 4 – At Bend and Bench on NMR down from Braddock Trail intersection

Not much vegetation exists on the left bank due to the trail and frequent stream access. This degradation promotes accelerated run-off into this site. However, the right bank is populated with high grass, ragweed, and various other small shrubs. Watercolor at this site is usually clear to cloudy depending on flow and weather conditions.

1.1.5 Site 5 – Adjacent to Walking Bridge on NMR

Site 5 is approximately 150 yards upstream of site 4 on Nine Mile Run, and is shown in **Figure 1-6**. This site is closest site to the culverted section of NMR, and was selected to evaluate the affect of the Homewood CSO, and SSOs from Edgewood and Swissvale. Site 5 is also adjacent to a gravel walking path and wooden bridge. Going upstream from site 4, the width of Nine Mile

Run bottlenecks to half the size of site 4. This bottleneck increases flow velocity through this section creating a deeper channel than the previous site.



Figure 1-6: Site 5 - Adjacent to Wooden Walking Bridge on NMR

Flow varies through the cross-section of this site due to positioning and accumulation of rocks. Small amounts of leaves were observed at this site, but the site remains mostly clear of debris. Both banks are rocky and heavily vegetated with high grass and small shrubs. The low-lying right bank in the background of **Figure 1-6** serves as a floodplain at this site and is susceptible to frequent flooding. The sources of contamination at this site include sediment from the walking path, urban runoff from the I-376 highway and the Edgewood and Swissvale neighborhoods, and CSOs and Sanitary Sewer Overflows (SSO) from the Wilkinsburg Culvert.

1.1.6 Site 6 – Fern Hollow Park Bridge Crossing

Lancaster Avenue runs down into Frick Park and crosses site 6 via a foot or vehicular bridge. This site is on a tributary to NMR called Fern Hollow, which is routed beneath the bridge through a concrete conduit shown in **Figure 1-7**. Fern Hollow is a small stream that borders the Edgewood neighborhood next to Frick Park. Flow in this section of stream can become very low and partially dry up during drought conditions. The section of Fern Hollow immediately upstream of this site flows through a wetland where Falls Ravine creek intersects.



Figure 1-7: Site 6 - Outflow From Under Park Road Bridge on Fern Hollow

The sampling area is at the outflow of a concrete pipe that goes under a park road. This site was chosen to look the potential affect of road salt usage within the park, as well as providing a comparison as the most downstream site on Fern Hollow. Flow at the site is very

slow, under most conditions, and the water is frequently stagnant and very turbid. The lack of flow provides ideal conditions for buildup of leaves and other debris. A pungent odor was observed at this site, presumably due to the alternative decomposition of large amounts of decaying natural organic matter (NOM). In addition to NOM, the entrance of the park road and the vehicles that use it are the main sources of contamination at this site. The park road branches from Lancaster Avenue, funnels down a steep hill, and ends at a loop by the Tranquil Trail soccer fields, is the only paved public road that enters the Park. Bank conditions on both sides are a stable gradual slope with a mix of loose rock and large amounts of grass and weeds.

1.1.7 Site 7 – Falls Ravine Creek

Site 7 is approximately up the Falls Ravine Trail 200 yards on the left from the intersection of the Tranquil and Falls Ravine Trails. The Falls Ravine Trail bisects the center of Frick Park. Site 7 is on Falls Ravine Creek, which is spring-fed at its source, and will act as the fresh water control throughout the study. The actual location of this site was moved downstream from the previous years site due to significant erosion, flood damage, and subsequent repair that occurred from a snowstorm during the winter of 2009-10. The sampling point is downstream of the dilapidated bridge shown below in **Figure 1-8**. The entire Falls Ravine Trail was restored and partially re-routed with the use of heavy equipment during the spring of 2010.



Figure 1-8: Site 7 – Downstream of Dilapidated Bridge on Falls Ravine

Sand, wood, and other building materials were brought for this effort to restore the trail and partially divert stream flow through new drainage pipes. Because of the construction, large amounts of slate and coarse rock partially blocked flow into the sampling pool during Fall 2011. This created non-existent flow, which trapped debris and leaves until channelization took place in November of 2011. Both banks are steep and cut into a slate-type rock underneath the dilapidated wooden footbridge. Since this stream bisects the center of the park, is spring-fed, has no tributaries, and sees no vehicle traffic, the water here is hypothesized to have base line water quality to compare the other sites.

1.1.8 Site 8 – Fern Hollow Beneath Forbes Avenue Bridge

Site 8 is 20 yards upstream of the Hot Dog Dam and is shown in **Figure 1-9**. It is also approximately 400 yards upstream of site 12. This site was selected to help quantify contamination from vehicle traffic and the drainage pipe that is pictured in the left of **Figure 1-9**. Large volumes of automobiles travel the overlying Forbes Avenue Bridge on a daily basis and can create runoff of roadside debris. This site also provides an important comparison to site 12 to help determine pet pollution because of its location 20 yards upstream of the Hot Dog Dam. The Hot Dog Dam is a wood and rock dam that creates a deep pool of water for dogs to bath and swim in. Flow at this site is reliably fast and low at all times of the year with good water clarity. Leaves and other debris do not usually accumulate at this site due to the fast flow but trash is seen occasionally because of the Forbes Bridge and high traffic pedestrian area. Both sides of the bank consist of loose rock and small boulders that help bank stability.



Figure 1-9: Site 8 – Below Forbes Bridge and Upstream of Hot Dog Dam on Fern Hollow

1.1.9 Site 9 – Drainage Pool Adjacent to Tranquil Trail

A small runoff from an adjacent hill feeds a pool that is neatly surrounded by large rocks, which is sampling site 9 in **Figure 1-10**. An upstream site does not exist above site 9, but the outflow does feed into Fern Hollow Creek. Site 9 was chosen to evaluate fecal contamination because dogs are frequently observed swimming and walking around the site area. This site layout is unique because it is the only site that flows directly into a drainage grate. The run-off into this pool comes from a large garden area located along Forbes Avenue.



Figure 1-10: Site 9 – Drainage Pool That Flows Into Fern Hollow

The pool flows into a drainage grate seen at the base of **Figure 1-10**. The drainage grate then diverts the flow of water underneath the Tranquil Trail and into Fern Hollow above site 8. Since this site is a 0.5 meter deep pool, very little flow is observed and the water is always turbid due to suspended sediment and frequent agitation by pets. Also, due to the restriction of the grate, this site is optimal for retaining large amounts of leaves and other NOM. Exit and entrance flows are consistent and are primarily driven by precipitation events. Besides the rocks lining the pool, the banks consist ample amounts of grass, small shrubs, and an assortment of trees.

1.1.10 Site 10 – Tranquil and Homewood Trail Intersection on Fern Hollow

A stone arch that encloses a concrete conduit that passes underneath the intersection of the Tranquil and Homewood Trails. A pool exists at the outflow of the conduit, which is Site 10. It is across the Tranquil Trail from site 9 and is shown in **Figure 1-11**. As it can be seen in **Figure 1-11**, this site tends to backup due to the restriction of leaves, soil, and other debris. Fern Hollow flows out from the pipe in **Figure 1-11**, and intersects the outflow of site 9 before flowing down to site 8.



Figure 1-11: Site 10 – Outflow of Homewood Trail Bridge on Fern Hollow

Depending on flow and weather conditions, this site varies from very cloudy when stagnant, to clear when some flow is present. Site 10 was selected upstream of site 8 to provide data for water above the Forbes Bridge and pipe outflow. Both banks follow a similar gradual profile with no rocks sparse vegetation.

1.1.11 Site 12 – Downstream of Hot Dog Dam on Fern Hollow

Site 12 is on Fern Hollow immediately upstream of the Biddle Trail footbridge. **Figure 1-12** shows site 12, which is downstream from site 8 as well as the Hot Dog Dam. Sample site 12 was delineated to help quantify pet pollution in coordination with site 8. The section of stream between this site and site 8 meanders through a very flat floodplain that sometimes creates a network of braided channels. This site was selected to evaluate fecal contamination resulting from the Hot Dog Dam on the section of Fern Hollow below site 8. Because of the flat profile,

flow is slow and constant. The water is typically clear and shallow (0.1 meters). Samples were taken from the center of the channel before a footbridge on the Biddle Trail. Because of the fairly new bridge, various construction materials and excess soil have been observed adjacent the site. Both banks are of similar slope and consist of a slate-type rock deposit.



Figure 1-12: Site 12 – Upstream of Biddle Trail Bridge on Fern Hollow

2.0 STATEMENT OF THE PROBLEM

Nine Mile Run runs through the largest park in the City of Pittsburgh and gets thousands of visitors per day, thus it is necessary to establish a baseline of pollutants and identify potential sources within the watershed that can impair water quality. Through monitoring efforts, it can be determined if the water quality were compromised in a fashion that may have an affect on the public health of the region, cause a decrease in park usage, and lead to aesthetic problems and impairment to already existent restoration features. Several eyewitness accounts of children and young adults playing in Frick Park streams were observed throughout the duration of the study. While playing, the children were unsupervised and had their hands and feet in the water. It is circumstances like these that have the potential to be harmful to the health of individuals that are exposed to the water.

The parameters measured in this study will help to postulate linkages to potential causes of water quality degradation, as well as provide data and evidence for future grants and park infrastructure improvements. An analysis of the water quality within Frick Park is presented herein to provide insight into the effect that the below contamination sources have on the public health and aesthetic quality of Frick Park. An in depth analysis of water quality involving an expanded set of 11 sites on NMR, Falls Ravine, and Fern Hollow was performed over the course of 8 months. Several sources of contamination considered throughout the study include:

- Deicing agents used on roads in the winter

- Suspended solids, heavy metals, major anions, and bacteria concentrations from CSO, Sanitary Sewer Overflows (SSOs), and Storm Sewers
- Pathogenic Bacteria from fecal matter

Examples of contamination sources observed during sampling are shown below in **Figure 2-1** and **Figure 2-2**. **Figure 2-1** shows a dead rat at the CSO outflow, which is sampling site 1. The dead rat in **Figure 2-1** is just one example of the environmental and health risks that can result from a CSO in the form of infectious disease or bacteria. In addition to dead animals, large amounts of trash in the form of diapers, empty bottles, food containers, and plastic wrappers were found in the CSO site during samplings. **Figure 2-2** depicts two dogs in the Hot Dog Dam area of Fern Hollow in-between sites 8 and 12. Dogs were observed in park streams during several samplings and during regular park use. Fecal contamination from animals and humans is an important issue in the Frick Park ecosystem, and because Nine Mile Run and its tributaries eventually flow into the Monongahela River, it can affect the drinking water of the region and areas downstream. This work aimed to associate these sources of contamination with the bimonthly lab and field measurements taken from the Frick Park watershed.



Figure 2-1: Contamination at Combined Sewer Overflow Site



Figure 2-2: Source of Contamination in Hot Dog Dam on Fern Hollow

2.1 POSSIBLE CONTAMINANTS

2.1.1 Deicing Agents

Deicing agents can have adverse effects on the aquatic life in a receiving surface water body, and the close proximity of I-376, city, and park roads to Nine Mile Run Watershed make this type of contamination a possibility. An average of 42 inches of snow falls in the Pittsburgh region each year meaning that salt and various other deicing agents (MgCl_2 , and CaCl_2) are used to keep roads clear and passable for commuters during the winter months (PennDOT, 2010b). The area is also located in a very hilly “ice belt,” where repeated and copious applications of deicing salts in winter months would be anticipated (Korkak *et al.*, 2001a). Frick Park resides in PennDOT’s district 11, which is comprised of Lawrence, Beaver, and Allegheny counties. In Allegheny County alone, there are 3,322 miles of snow lanes. During the winter of 2009-2010, Allegheny County used 49,541 tons of salt and 340,151 gallons of brine (PennDOT, 2010b). This breaks down to 14.9 tons (51,139 lbs) of salt per snow mile lane within the County. PennDOT mainly uses 100% salt (NaCl) and antiskid (mix of tiny stones and sand) on all interstate highways, major expressways, and heavily travelled roads. The primary function of salt is to melt snow and ice, and is primarily effective when applied at temperatures above 20°F. An anti-icing program is also utilized in the area to enhance melting capacity of salt in extremely cold temperatures. Several chemical compounds are used in this anti-icing program including liquid forms of MgCl_2 , and CaCl_2 , which prevent precipitation from forming a strong bond with the pavement (PennDOT, 2010a).

PennDOT has a road classification breakdown based on traffic volumes and priorities. Type A and B roads are treated first during winter events because they carry the most traffic. Type C roads are treated in a similar fashion to B because of the high volumes of traffic in the

morning and evening rush hours. State highways within Pennsylvania are classified into the following six categories (PennDOT, 2010a).

- Type A: Interstate Highways (I95 and I76)
- Type B: Other expressways and Principal Arterials
- Type C: Minor Arterial Highways/Heavily Traveled local roads (US 30)
- Type D: Collector Highways (Rural routes with light to moderate traffic)
- Type E: Local Access highways
- Type F: Ramps

Based on this classification, I-376 highway would be a PennDOT classified Type A road, suggesting that it sees the highest application of salt content and represents the southern border of Frick Park. The five NMR sampling sites in this study all reside within a 0.80 mile stream section that parallels the I-376 highway before crossing under Commercial Avenue and the Squirrel Hill Tunnel. Adjacent topography between the urbanized highway area and the stream basin is a fairly steep bank causing runoff to channel contaminated water directly to NMR. Given this exposure, high cation concentrations (Na^+ , Ca^{2+} , Mg^{2+}) and anionic chloride would be expected in NMR because most of the salt that is placed on roadways during snow and ice operations runs off with other roadway drainage. According to American Association of State Highway and Transportation Officials (AASHTO), approximately 55% of road salt chlorides are transported in surface runoff with the remaining 45% infiltrating through the soils and into groundwater aquifers (Verner Consulting and Parsons Brinkerhoff, 2004). Although groundwater infiltration is highly dependent on local conditions, runoff from the surrounding urbanized landscape likely feeds into NMR causing salt to remain in solution. Once present in the surface water, chloride is not subjected to a natural removal mechanism and has the potential

to infiltrate the groundwater. Spikes in deicing agents can cause an accumulation and persistence in watersheds, yielding a potential risk to aquatic ecosystems and water quality (Verner Consulting and Parsons Brinkerhoff, 2004). These risks include increased corrosiveness due to an increase in electrical conductivity, as well as associated high levels of sodium that can cause human health affects like hypertension. Research by the Colorado Department of Transportation has shown that NaCl, MgCl₂, and CaCl₂ may contribute to the mobilization of trace metals from the soil to surface and groundwater, while chloride in deicers can increase the salinity of the receiving water body (Verner Consulting and Parsons Brinkerhoff, 2004). A previous study was observed involving ion exchange, in combination with the formation of chloride complexes, to mobilize zinc and cadmium (Backstrom *et al.*, 2004). These conclusions were confirmed in surface waters adjacent to roads that were deiced with NaCl (Backstrom *et al.*, 2004). Overall, deicing agents have significant environmental drawbacks including damage to roadside and riparian vegetation, pollution of wells and surface water, and damage to hydraulic properties of roadside soils. This study will provide a correlation of deicing use and time of year, to fluctuations in water quality. The implication of pollution due to deicing agents in Frick Park has the potential to impair the water quality and aquatic life of the Nine Mile Run Watershed.

2.1.2 Combined Sewer Overflows (CSO) and Sanitary Sewer Overflows (SSO)

Water quality within the NMR Watershed is adversely affected by sewage inputs from combined sewer overflows (CSOs), sanitary sewer overflows (SSOs), and discharges from storm water sewers. Another concern stems from unauthorized sewer discharges into the culverted section of NMR (Collins *et al.*, 1998). A CSO is a combined sewer system that carries both sewage and

stormwater runoff, and is designed to overflow to natural surface waters (i.e. NMR) in the event of overloading (Collins *et al.*, 1998). Sanitary sewers are usually smaller (15.24-50.8 cm diameter) and carry household waste to a water treatment facility, while storm sewers funnel stormwater runoff to the nearest receiving surface water (Collins *et al.*, 1998).

Pittsburgh and the area surrounding the NMR Watershed is served by combined, sanitary, and storm sewers. These systems usually consist of sewer flow to an interceptor sewer and later to a wastewater treatment plant under dry weather conditions. However, during wet weather events, a combined flow regulator structure diverts a portion of the flow to a receiving stream like NMR (NMRWA, 2011). During both wet and dry weather conditions, the capacity of the CSO is often exceeded and a mixture of sanitary sewage and storm water is discharged into receiving waters at CSO outfalls, *i.e.* site 1. These wet weather events represent a large input of nutrients, organic matter, pathogens, bacteria, contaminants, and debris to a receiving waterway (El. Samrani *et al.*, 2008). According to the United States Environmental Protection Agency (USEPA), the City of Pittsburgh has 194 total CSO outfalls, with six of these CSO outfalls discharging directly into NMR (USEPA, 2011b and Collins *et al.*, 1998). Only one of these six CSOs occurs within the sampling area selected for this study. It is a box culvert that flows along Fern Hollow before merging directly into NMR just upstream of Commercial Avenue. However, the culverted section of NMR above the Braddock Avenue outflow receives CSO input from the Homewood section of the city of Pittsburgh 1.5 miles away (Collins *et al.*, 1998). Also adding diluted raw sewage input into upper NMR are three SSO diversion structures at the mouth of the Wilksburg Culvert, two of which are from Edgewood and one is from Swissvale (Collins *et al.*, 1998). The input from the Homewood CSO, Edgewood and Swissvale SSOs, and

NMR CSO outfall could degrade the water quality of NMR throughout the entire sampling area by the discharge of raw sewage.

The surrounding urbanized terrain and steep slopes in the Frick Park area provide ideal conditions for high runoff flow rates that cause contamination from CSOs and SSOs. Also, due to the relatively small footprint of NMR, CSOs can be a significant pollutant source contributing to poor water quality within the Nine Mile Run Watershed and the surrounding area. Pollutants from sewer systems can be attributed to runoff, sanitary sewage, and erosion of sewer sediments that persist in the system for long periods of time (Gromaire *et al.*, 2001). Known indicators of CSO pollution include increased levels of suspended solids concentration, heavy metal concentration, anion concentrations, fecal coliform, enterococci, and E. Coli counts. In addition to lab tests, field measurements of turbidity, pH, and DO will be recorded to better quantify the effects of the CSO. A CSO would be expected to provide a lower pH during weak rain events, because during storm events, the sanitary sewage will be more diluted by the higher influx of storm water. Quantification of the aforementioned constituents in the NMR Watershed provided a solid baseline for the contribution of pollution resulting from the surrounding sewer system.

2.1.3 Fecal Contamination

Quantification of fecal contamination in Frick Park is important for the usability and public health of the surrounding area. Fecal pollution of a receiving water body will lead to the transmission of pathogens. These pathogens cause waterborne diseases such as diarrhea, cramps, nausea, headaches, or other symptoms. E. Coli and enterococci are fecal indicators whose occurrence indicates that water may be polluted with a form of human or animal waste. Sources of fecal contamination can be point and non-point sources. Point sources include raw sewage

from leaking sewer pipes, storm water, CSO outflows, or industrial sources. Non-point sources would be attributed to animals, or urban run-off (Savichtcheva and Okabe, 2006). Sites 1 and 12 were projected to have the highest fecal contamination due to the outfall of the CSO, and pollution from dogs when compared to the rest of the sites in this study. Animal feces may contain a variety of pathogenic microorganisms such as, Salmonella, some protozoa, and several virus groups (CDC, 2010). Due to the close proximity of Frick Park to several urban neighborhoods, fecal contamination due to dogs, wildlife, and humans is an important concern to the children that play in the streams. Dog contamination, especially, needs to be evaluated because of dog friendly atmosphere in Frick Park.

Water and Wastewater treatment facilities use total coliforms, fecal coliforms, E. Coli, and enterococci as bacterial indicators in water quality and health risk assessments. These bacteria are normally present in the intestines and feces of warm-blooded mammals, including wildlife, livestock, and humans (Meays *et al.*, 2004). E. Coli and enterococci were tested throughout this study due to their usefulness as indicator organisms. The detection of E. Coli is much easier and less costly than the pathogens themselves. Enterococcus has been used for years in many countries as a monitoring tool for microbiological impairment of water and for prediction of the presence of bacterial, viral, and protozoan pathogens (Savichtcheva and Okabe, 2006). This issue is imperative to quantify and pinpoint because excessive bacterial contamination can pose health risks to recreational users of the NMR Watershed. If the origin of fecal contamination and pathogens can be correctly identified, management and remediation efforts can be instituted to alleviate and prevent possible future outbreaks or limit on-going contamination.

3.0 METHODS AND INSTRUMENTATION

A combination of field and laboratory based measurements were employed to evaluate the different water quality parameters that are of interest. Measurements were performed in the field to avoid possible loss of information or immediate changes that may be associated with storage and handling. Other more stable parameters were measured later in the laboratory and were stored according to widely accepted methods.

3.1 FIELD MEASUREMENTS

Immediately upon sample procurement, field measurements of dissolved oxygen (DO), pH, total dissolved solids (TDS), and temperature were recorded. These measurements were combined with observations such as water depth and color, barometric pressure, 24-48 hour precipitation, and ambient temperature to allow for an initial judgment of water quality on a particular sampling day. A Cole Parmer Digi-Sense pH/ATC/mV/temp meter was the primary field instrument used. DO and pH were measured by switching out accessory instruments specific to each property. The DO was measured using an Orion 97-08-00 O₂ electrode with the pH option selected on the Digi-Sense. Prior to use, the DO electrode was calibrated with DI water in a glass calibration bottle. The battery and ambient air pressure were also standardized with this instrument prior to use. To measure pH, the Orion electrode was swapped out for a 910500

Orion combination pH meter. It was calibrated using buffered pH standards. To provide a comparison to the TDS measurements that were done in the lab, a HM Digital TDS EZ meter was used to record field measurements.

3.2 LAB MEASUREMENTS

In addition to the aforementioned field measurements, several lab-based parameters were measured to evaluate the surface water quality in Frick Park. Parameters included, turbidity (NTU), total dissolved solids (TDS), total solids (TS), total suspended solids (TSS), Enterococci, E. Coli, Heterotrophic bacteria plate counts, and cation and anion concentrations. All procedures followed AWWA or EPA Standard Methods. These parameters were selected because they covered a broad range of potential contaminants that may be present in Frick Park.

3.2.1 Turbidity

Turbidity pertains to an optical property of materials in water that causes light to be scattered and absorbed instead of being transmitted in straight lines through a sample. Turbidity is a result of suspended matter, such as clay, silt, finely divided organic and inorganic matter, soluble organic compounds, and microscopic organisms that are present in a water sample. The standards and measurements for turbidity are in nephelometric turbidity units (NTU). The clarity of the water is very important when it is the source for drinking and industrial uses, as well as when trying to link possible sources of contamination. Higher turbidity levels can also be associated with increased levels of viruses, bacteria, and other pathogens that adsorb to the suspended particles. In surface water, turbidity may be caused by phytoplankton, high sediment loads from storms,

erosion, or construction, mining operations, and runoff from roads, bridges, and parking lots. In the case of this study, the highly urbanized impermeable surfaces surrounding Frick Park promote flash flooding, which increase the turbidity levels during these time periods.

Turbidity is measured when light is scattered by particles in the sample and detected by a sensitive photomultiplier tube at a 90° angle from the incident light beam. The amount of light that reaches the photomultiplier tube is proportional to the sample turbidity (AWWA *et al.*, 1998a). An electrical signal is created by a conversion of light energy that is amplified and displayed on the instrument meter. To provide the most accurate results, a light shield is used to cover the sample during the test to prohibit external light, and trap the light within the instrument that is passing through the sample. Measurements throughout the study were performed using the Hach 2100 A Turbidimeter, which is shown in **Figure 3-1**.



Figure 3-1: Hach 2100 A Turbidimeter and Standards 0.61-1000 NTU

The first step in using the Hach 2100 A was to turn the meter on in the 1-1000 NTU range for 30 minutes prior to use to allow the lamp to warm and achieve equilibrium. Each standard tube was then wiped clean with a Kimwipe. The sample tube was also cleaned with deionized (DI) water before addition and measurement of each sample. Once the Turbidimeter was warmed up, it was calibrated by selecting one of the four standards (0.61, 10, 100, 1000 NTU) closest to the sample quality. If the 100 NTU standard cell most closely represented the sample, it was inserted into the sample compartment and covered with the light shield. The range selector switch was then changed to 0-100 NTU and the calibration knob was adjusted to attain 100 NTU on the meter. Then, the 100 NTU standard was replaced with the 10 NTU standard cell producing a reading of 10 +/- 5 NTU (AWWA *et al.*, 1998a). Once the calibration steps were completed, the sample was inserted and results were recorded based on the 0-100 range. Samples that did not register values on the 0-100 scale were calibrated using the 10 or 0.61 NTU standards. This process was repeated for all samples.

3.2.2 Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) is regulated for aesthetic and health effect reasons. Elevated TDS in surface water in the United States can be associated with natural features such as, mineral springs, carbonate deposits, drinking water treatment chemicals, storm water runoff, and wastewater discharges. A limit of 500 mg of dissolved solids/L is desirable in drinking waters is the current set standard by the Secondary Drinking Water Standard (AWWA *et al.*, 1998a). “Dissolved solids” refer to any minerals, salts, metals, cations, or anions dissolved in the water. In regards to this study, known contributors to elevated TDS concentrations include salts from road deicing, combined sewer discharges, and animal waste runoff. TDS provides a qualitative

measure of the amount of dissolved ions, and is commonly used as an indicator test to determine the general quality of the water. Buildup of these dissolved ions could lead to corrosiveness in the water, salty or brackish taste, or result in scale buildup on pipes.

Various categories exist for solids in environmental samples. This study evaluated the terms defined as total solids, dissolved solids and suspended solids were measured. The process of measuring TDS is known as a gravimetric analysis, which is based on determination of constituents or categories of materials by a measurement of their weight. Therefore, TDS levels were calculated by subtracting the Total Solids (TS) from the Total Suspended Solids (TSS). The TS is the material residue left in a beaker after evaporation of a sample in an oven at 110 °C (AWWA *et al.*, 1998a). TSS is the portion of total solids retained on a filter, and TDS is the portion that passes through the filter, thus the difference between the two. Each sample is separated by general operations that include filtration and evaporation. The left over residue of each sample is weighed with an analytical balance (AWWA *et al.*, 1998a). Filtration separates suspended or particulate (non-filterable) fractions from dissolved or soluble (filterable) fractions. For this study, depth filters (Whatman glass/paper filters) were used, intercepting particles that penetrate a deep mat of fiber. After filtration, evaporation separates the water from dissolved or suspended material via an oven set at 103-105 °C. This temperature is used to maintain levels of organic matter that would otherwise be lost to volatilization and decomposition at higher evaporation temperatures.

The laboratory procedures that were used to obtain the TS and TSS are described as follows according to AWWA Standard Methods. For TS determinations, a 250 mL beaker was labeled for each sample. Each beaker was handled at all times with beaker tongs to avoid contamination that would increase their weights. The initial weight of the beaker was recorded

prior to addition of water. After the initial beaker weight was recorded, 100 mL of sample was added to the beaker. The beaker was then placed in an oven at 103-105 °C for several days until all water was evaporated. The beaker was then removed from the oven and placed in a desiccator until fully cooled. After cooling, the beaker and its contents were weighed. This final weight was subtracted from the initial weight, thus yielding the Total Solids weight.

The TSS technique incorporated a filtration apparatus that included a heavy walled erlynmyer filtration flask, a Gooch crucible, filter, rubber crucible holder, and a T-connector with hoses hooked up to a vacuum line. The filter used was a Whatman Glass Microfibre Filter (93-ALT 0.21 mm diameter). It was placed into an empty, clean Gooch crucible. 5 mL of DI water was then passed through the filter to ensure a good seal to the base of the Gooch crucible. The crucible was then removed and placed in the oven at 103-105 °C for 30 minutes to ensure that all moisture was dried from the filter. Then the crucible was put in a desiccator and allowed to cool for 15 minutes. After the crucible was completely cooled, an initial weight was recorded using a Mettler AE-50 scale. The Gooch crucible was then placed back into the crucible holder and 200 mL of sample was filtered through under suction to the vacuum line. Once all liquid was removed from the crucible, it was placed back into the oven with tongs. Again, the crucible was allowed to oven dry for 30 minutes and then transferred to the desiccator. Once fully dry after cooling for 15 minutes, the crucible was re-weighed using the same analytical balance as before. This final weight was subtracted from the initial weight to achieve the TSS value. Both final values of TSS and TS had to be normalized and put into acceptable units (g/mL). This was accomplished by dividing the final values by the amount of sample that was used (100 mL for TS and 200 mL for TSS) to put the values into units of mg/mL. Then, by multiplying by 1000, the units of g/mL were attained. Once all units were in the same form, TSS was subtracted from

TS for each sample equaling TDS values. This procedure was done after each sampling period for the duration of the study. A final TSS product showing the Gooch crucibles with dried filters is shown in **Figure 3-2**. The different conditions present at each site can be seen by the degrees of solid buildup on each filter.



Figure 3-2: Gooch Crucibles After Filtration and Drying Showing Various Concentrations of TSS

3.2.3 Measuring Bacteria Plates

The heterotrophic plate count (HPC), formerly standard plate count, is a procedure for estimating the number of live heterotrophic bacteria present from in a surface water source. Colonies can occur in the form of pairs, clusters, chains, or single cells, all of which are included in terms of “colony-forming units” (CFU) (AWWA *et al.*, 1998b). The final count depends on the type of

interaction between developing colonies. Media used was Difco Co. Plate Count Agar, which is a dehydrated and pre-mixed compound. This was prepared in a similar manner to the Enterococci media, which is described in the next section. Plate count agar is usually applied by three different methods, two of which, pour plate and streak plate methods, were used in this study. Both methods were used for the first set of samples. A 1:10 dilution was applied to the pour plate samples, which allowed for quantification of bacteria at each site. Streak plates were used to investigate bacteria colonies because the streak plate method gave a good isolation of colonies with adequate spacing. Out of the main two methods for streak plating, quadrant and radiant, the quadrant was selected during the procedure. The process of a quadrant streak method involves spreading the sample over a small area on the edge of the plate with a sterilized loop. From the edge of the first area, five to six streaks were made while remaining close to the edge of the plate. The loop was flamed again and allowed to cool for five seconds. Six to seven streaks were then made from the second streak area. The loop was again flamed prior to streaks three and four. The streak and pour plate results during October and November 2010 factored into the decision to use E. Coli and Enterococci plates for the duration of the study.

The preparation of the agar solution was similar to the process for the enterococci agar preparation. The Difco Co. Plate Count Agar contained the formula shown in **Table 3-1**.

Table 3-1: Formula for 250mL of Plate Count Agar at pH 7.0+/- 0.2

Component	Amount (g)
Pancreatic Digest of Casein	1.25
Yeast Extract	0.625
Dextrose	0.25
Agar	3.75

The Plate Count Agar solution was created by adding 6.9 g of agar into 250 mL of DI water. A stir bar was used as the mixing mechanism and aluminum foil was used to cover the top of the beaker once the solution was heated and fully mixed. The agar solution was then placed in the Market Forge Sterilmatic Autoclave for 30 minutes, which operates at 121 °C with an internal pressure of 15 psi. The samples were carefully removed using thermal gloves and protective eyewear due to the high temperatures and pressures that exist in the autoclave. Sterile pipets were then used to transfer 10 mL of the media from the beaker to corresponding labeled Petri dishes. The media was allowed to solidify and the water samples were diluted to or below 10% of their original volume. This was done because initial tests used raw water samples and proved to be un-readable due to colony overgrowth. Once the samples were diluted, a sterile loop was used to spread the water samples onto each plate according to the Quadrant streak method discussed above. Plates were then placed in an incubator at 35 °C for 24-48 hours. An example of three pour plates is shown below in **Figure 3-3** after an incubation time of 48 hours. The black dots on each plate represent a bacteria colony.

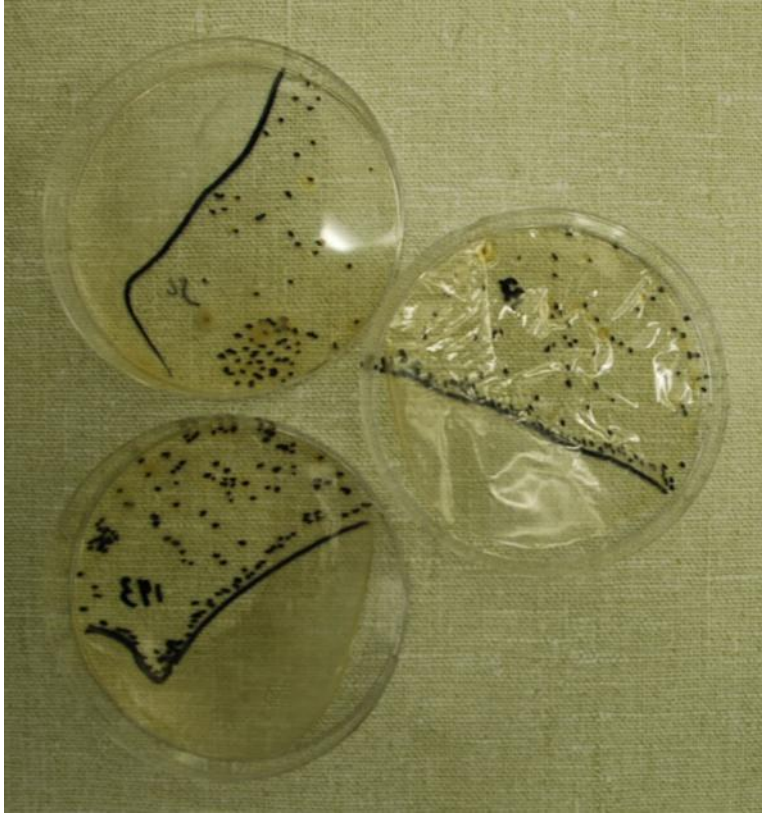


Figure 3-3: Heterotrophic Bacteria Plate Post-Incubation

During colony observation and data acquisition, shapes and colors of colonies were recording in the final count. After final colony counts were observed using Quebec and mechanical counting devices, the numbers of colonies per mL were calculated as the final values. HPC plates were performed only on October and November samples. This was done to verify the bacteria did indeed exist within the watershed. Once it was certain that bacteria were present, Enterococci and E. Coli Agars were selected for the remaining sampling dates to target specific types of bacteria.

3.2.4 Determination of Enterococci Bacteria by Membrane Filtration

The Enterococcus group is a subgroup of the fecal streptococci that includes *E. faecalis*, *E. faecium*, *E. gallinarum*, and *E. avium*. Enterococci differ from other streptococci by their ability to grow in 6.5% sodium chloride, at pH 9.6, and at 10 °C and 45 °C (AWWA *et al.*, 1998a). Thus, enterococci are a concern in various types of environments, especially in conditions where other bacteria might not exist. They are also important indicator organisms for determining the extent of fecal contamination of particular surface water. The correlation with fecal contamination has been used in studies at marine and fresh water beaches that indicate that swimming caused gastroenteritis is related directly to the quality of the water as predicted by enterococci levels (AWWA *et al.*, 1998a). Therefore, Enterococci are considered one of the most efficient bacterial indicators of water quality (AWWA *et al.*, 1998a). The guideline for fresh waters is 33 enterococci/100 mL based on the geometric mean of at least five samples per 30 days (AWWA *et al.*, 1998a).

Quantification of enterococci was performed using membrane filtration (MF). MF was chosen over most probable number (MPN) because it is preferred in the industry and requires less work. Prior to filtration, 150 mL of DI water was boiled in a beaker and 6.3 g of Bacto m-Enterococcus Agar (m-Azide Agar) was added and completely mixed. This agar was specifically developed for MF by Slanetz, and consists of the components showed below in **Table 3-2** (Slanetz and Bartley, 1957).

Table 3-2: Components for 150mL of m-Azide Agar

Component	Amount (g)
Tryptose	3.00
Yeast Extract	0.75
Dextrose	0.30
Dipotassium Phosphate	0.60
Sodium Azide	0.06
Agar	1.50
2, 3, 5 - Triphenyl tetrazolium chloride (TTC)	0.015

The 2, 3, 5-triphenyl tetrazolium chloride (TTC) is a dye that acts as an indicator of bacterial growth. TTC is reduced to insoluble formazan inside the bacterial cells and colors the colonies pink-dark red during the incubation process at 35 °C (Slanetz and Bartley, 1957). Once the solution reached a boil and was mixed thoroughly, 5 mL of the agar was dispensed into a 9 x 50 mm Petri dish via a sterile pipet. While the agar was cooling for 30 minutes, 100 mL samples were diluted to 10% of their original strength using DI water (10 mL sample/90 mL DI water). This was done because previous results with un-diluted water yielded un-countable high results. A sterilized Millipore™ filtration apparatus was used in conjunction with a sterile white Millipore™ 150 µm thick, 0.45 µm pore size, gridded filter disk. These filters are manufactured so bacteria larger than 0.47 µm cannot pass through, allowing determination of small numbers of bacteria in large volumes of water. Once all of the 100 mL samples were vacuum filtered, the filter was then transferred using sterile forceps to the surface of the sterile m-Enterococcus Agar medium in the Petri dish. This process was repeated for all samples as well as one blank (sterile control). Once successfully plated, they were placed in an incubator at 35 °C for 24-48 hours.

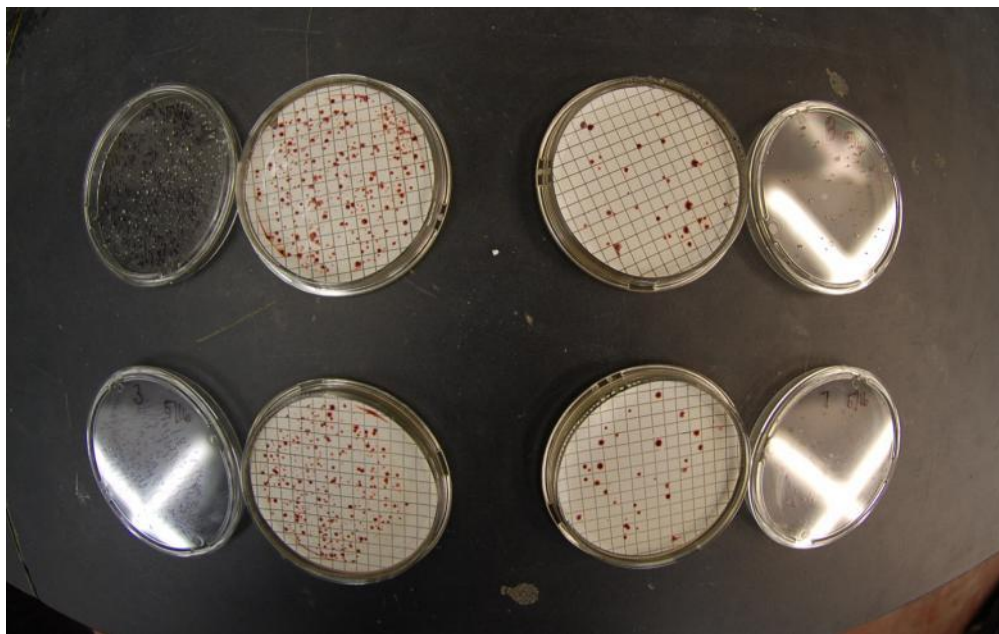


Figure 3-4: Enterococci Plated Samples Post-Incubation Showing NMR Sites on the Left and Sites 8 and 7 on the Right

Upon removal from the incubator, pink to dark red colonies were counted, calculated, and expressed as x-number of colonies per 100 mL sample. An example of samples plated on Enterococci Agar is shown above in **Figure 3-4**. Colonies are represented by the dark red dots seen within the grid. This Figure shows the variation that existed between Enterococci counts at each site. NMR sites are on the left while a Falls Ravine and Fern Hollow site are on the right.

3.2.5 Determination of Escherichia Coli (E. Coli) by Membrane Filtration

The determination of E. Coli bacteria followed Standard Methods and the same procedures as Enterococci in regards to the membrane filtration method, Petri dish size, incubation period, counting procedure, and filter type. The only variation was media preparation in which the E.

Coli agar required an autoclave. Difco-m TEC Agar was selected and the following **Table 3-3** shows the components that are contained in 100 mL of water.

Table 3-3: Components for 100mL of m TEC Agar Used for E. Coli Samples

Component	Amount (g)
Preteose Peptone No. 3	0.50
Yeast Extract	0.30
Lactose	1.00
Sodium Chloride	0.75
Monopotassium Phosphate	0.10
Dipotassium Phosphate	0.33
Sodium Lauryl Sulfate	0.020
Sodium Desoxycholate	0.010
Bromcresol Purple	0.008
Brophenol Red	0.008
Agar	1.50

The acronym m-TEC stands for “membrane thermotolerant E. coli.” Like Enterococci, E. Coli is widely used as an indicator of fecal pollution in water (Acumedia, 2011). It is a member of the fecal coliform group and is predominantly found in the fecal material of warm-blooded animals (Acumedia, 2011). As stated above, the only difference between this procedure and that of the Enterococci plating technique, is the use of the autoclave. When prepared, the m-TEC agar is a deep purple color that is slightly opalescent. After incubation and the addition of filter samples, yellow to yellow-brown colonies distinguished the presence of E. coli. The color change from deep purple to yellow-brown can be seen in **Figure 3-5**. The top portion of the Figure includes a blank sample and six other samples from left to right. The bottom portion of **Figure 3-5** depicts a close-up of two samples from different sites. A distinct difference in color can be observed between the left and right two samples. The right two samples are clearly inundated entirely

with E. Coli while the left two have bacteria present, but only a few of which are E. Coli colonies. Final colony counts were multiplied by a factor of 10 because of the 10% initial dilution of samples.

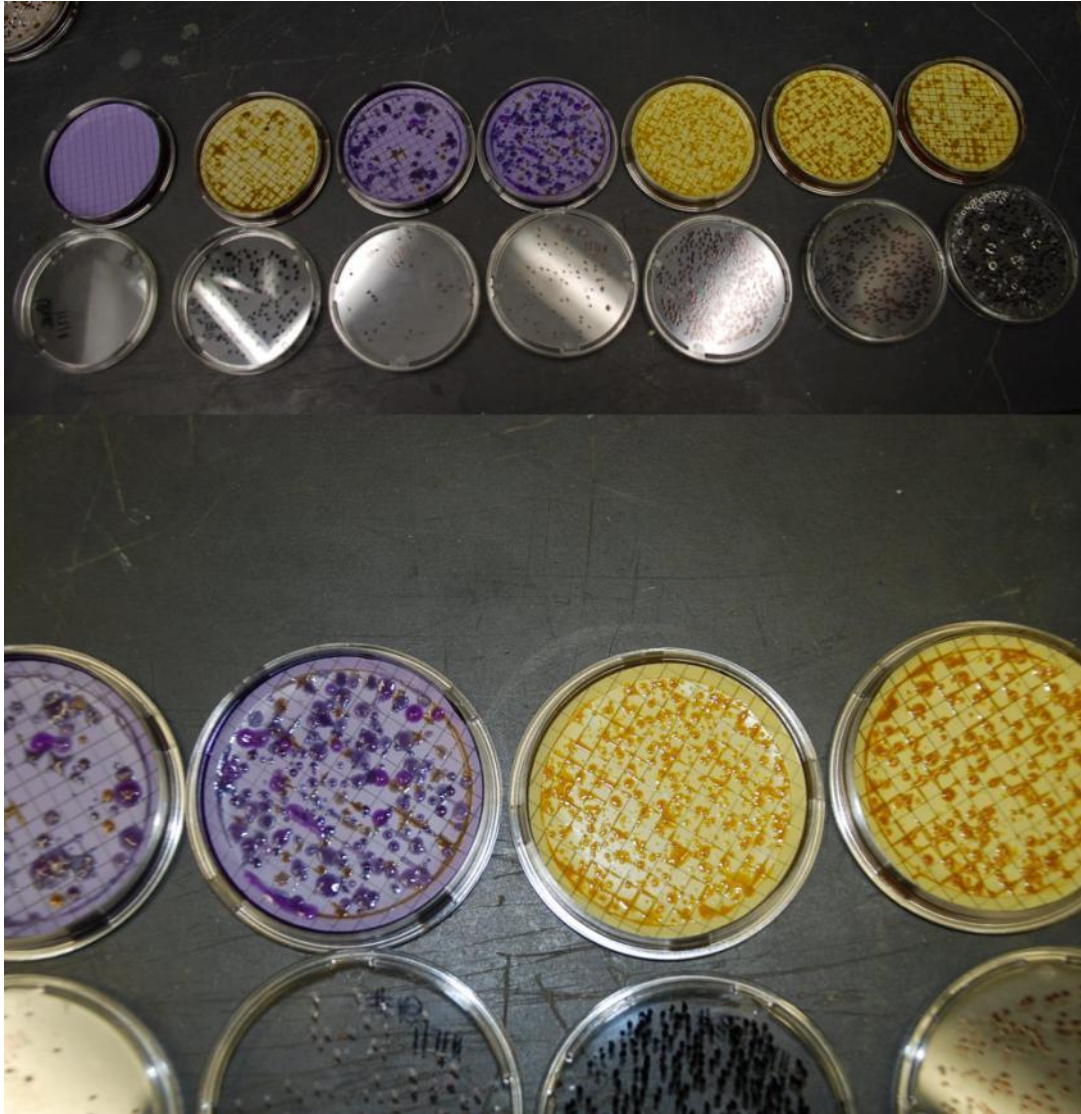


Figure 3-5: Coli Plated Samples Post Incubation Showing E. Coli Negative (Left) and Positive (Right) Samples

3.2.6 Atomic Absorption Spectrometry

Atomic absorption (AA) spectroscopy works by aspirating a dilute aqueous acidic sample solution containing metal into a flame within an atomic absorption spectrophotometer and detecting the absorbance as a function of solution combination. While in the flame, the solution is atomized just above the tip of the burner, resulting in finely separated solid particles that are transported to a region in the center of the flame (Perkin Elmer Co., 1988). This is the hottest portion of the flame causing the solid particles to form into gaseous atoms. Excitations of atoms also occur in this region moving from a grounded to excited state with the aid of a specific wavelength of light energy. With an increasing number of atoms in the light path, the amount of light absorbed also increases. A quantitative determination of the metal concentration is made by measuring the amount of absorbed light using a specific light source and careful selection of wavelengths, which target various metals and individual elements (Perkin Elmer Co., 1988). The concentration values were determined using a Perkin Elmer Model 1100B single beam atomic absorption spectrophotometer. A photo of the spectrophotometer used during the study is shown in **Figure 3-6**.



Figure 3-6: Perkin Elmer Model 1100B Atomic Absorption Spectrophotometer Used to Find Concentration Values of Cationic Species

It uses a hollow cathode lamp to emit a spectrum specific to an element, which is focused through a sample cell into the monochromator (Perkin Elmer Co., 1988). The monochromator disperses the light and the specific wavelength of isolated light passes to the detector. As part of the analysis, a calibration curve determining the relationship of absorbed light and the standard solution concentrations is created to define the actual metal concentration of the sample solution.

Since atoms absorb light at specific wavelengths it was necessary to use a different hollow cathode lamp for each individual element. A cathode lamp represents a bright, stable narrow-line source for most elements in the form of a hollowed-out cylinder constructed with a desired metal (Perkin Elmer Co., 1988). The anode and cathode are housed in a glass cylinder that is filled with neon or argon (Perkin Elmer Co., 1988). Acetylene or oxygen is selected as the fill gas based on the element being tested. An example of a potassium cathode lamp loaded

into the HCL1 plug on the Perkin Elmer Model 1100B is shown in **Figure 3-7**. There are two HCL plugs that correspond to two different lamp ports that can be utilized on the machine. For example, the potassium lamp is in port 1 and plugged into HCL1 in **Figure 3-7**.



Figure 3-7: Potassium Cathode Lamp in the Perkin Elmer Model 1100B Plugged Into HCL1 and Port 1

Nine elements of interest were selected based on previous studies and overall relevance to the sampling areas. The selected elements were iron, calcium, aluminum, sodium, lead, zinc, cadmium, potassium, and magnesium. Iron, aluminum, lead, zinc, and cadmium were not measured after three months of data acquisition because the levels detected were below that of concern. Therefore, the entire study duration included testing for calcium, magnesium, sodium, and potassium, which are commonly associated with deicing agents and subsurface stratigraphy.

Concentration levels of these four elements will help evaluate the degree of contamination caused by deicing agents.

Two different flame parameters were used for the atomic absorption spectrophotometer depending on the type of metal being measured. For this study two fuel-oxidant combinations were used; the gas/air and the acetylene/air, which achieve at 1700-1900 °C and 2100-2400 °C respectively. Prior to AA use, each sample was filtered using 0.45 µm filters. The filters were placed in a Millipore flask apparatus with an applied vacuum. Used 0.45 µm filters are shown below in **Figure 3-8** after 100 mL of sample was passed through the Millipore apparatus.



Figure 3-8: 0.45µm Filters After Filtering 100mL of Sample. Darker Color Caused by High Concentrations of Suspended Sediment

Filtered samples were then poured into a small plastic bottle. Each filtered sample was diluted to 10% of its original strength for quantification of highly concentrated metals. The AA was turned

on to allow the hollow cathode lamp to warm-up and reach constant emission intensity. A lamp for each metal was selected and placed into one of four machine ports. The wavelength and current used for each element followed the default operating condition as suggested by the Standard Methods. The instrument was operated such to maximize signal detection. Once the maximum level was achieved, the air and flame were turned on, ensuring no leaks were occurring in, or around the burner head/lock ring. Three standards for each element were measured allowing the machine to develop a baseline curve. Standards were measured and recorded at several times during sample measurement to ensure consistent results.

3.2.7 Chloride Combination Ion Selective Electrode (ISE)

A chloride ion selective electrode (ISE) was used as a reference to chloride concentration data generated from the Ion Chromatograph (IC). The chloride electrode accurately measured the chloride ion followed similar magnitudes seen using the IC. The operation of the electrode is based on the potential that develops across a chloride-specific membrane. This potential is proportional to the activity of chloride ions in contact with the membrane (Fisher Scientific, 2007). A calibration curve was generated by reading the millivolt (mV) potentials of chloride standard solutions of 10, 100, 1,000, and 10,000 ppm with the chloride electrode. A subsequent plot of concentration on the log scale (x-axis) and mV on the linear scale (y-axis) yielded calibration curves used to convert mV readings to concentration (ppm).

The use of the ISE was done according to Standard Methods. Prior to ISE measurement, each sample was filtered using 0.45 μm filters. Individual filtered samples were measured by placing the electrode into the sample bottle and stirring at a moderate rate until mV reading

became stable. Between measurements, the electrode was removed, rinsed with DI water, and blotted dry.

3.2.8 Ion Chromatograph (IC)

Ion Chromatography (IC) was used to determine chloride, nitrate, and sulfate levels in the samples. Phosphate concentrations were below the detection limit for all samples. A Dionex 4500i IC was the instrument used throughout the study and is shown in **Figure 3-9**.



Figure 3-9: Dionex 4500i Ion Chromatograph

All samples were run over the course of 3 days (5/20/11, 5/23/11, and 5/25/11). There were 77 samples (7 sampling periods) analyzed using the IC dating back to December 2010. This provided a broad range of conditions including heavy snowfall and winter conditions, high flow event, and dry, warm weather. The operating conditions used for the Dionex 4500i Ion Chromatograph are listed in **Table 3-4**. Fresh eluent and regenerate solutions were mixed before sample production runs to ensure consistent results.

Table 3-4: IC Operating Conditions For the Dionex 4500i Ion Chromatograph

IC Conditions	
Eluent	1.80 mM Sodium Carbonate
Eluent	1.70 mM Sodium Bicarbonate
Regenerate	25 mN Sulfuric Acid
Run Time	11 minutes
Flow Rate	2.0 mL/min
Injection Volume	3-5 mL
Backpressure	980-1100 psi
Deionized Water	0.22 um Filtered
Conductivity Detector	CDM 2

Prior to sample runs, the IC was sparged for 8-10 minutes and a blank system sample was run as a baseline. Since 3 days of sampling took place, standards were run each day for chloride (60, 300, 600 ppm), nitrate (25, 50, 100 ppm), and sulfate (12, 40, 60 ppm) to ensure reproducible results. The standards were used to generate curves to calculate the concentration of anions in each sample. An example of a Chloride calibration curve is shown in **Figure 3-10**.

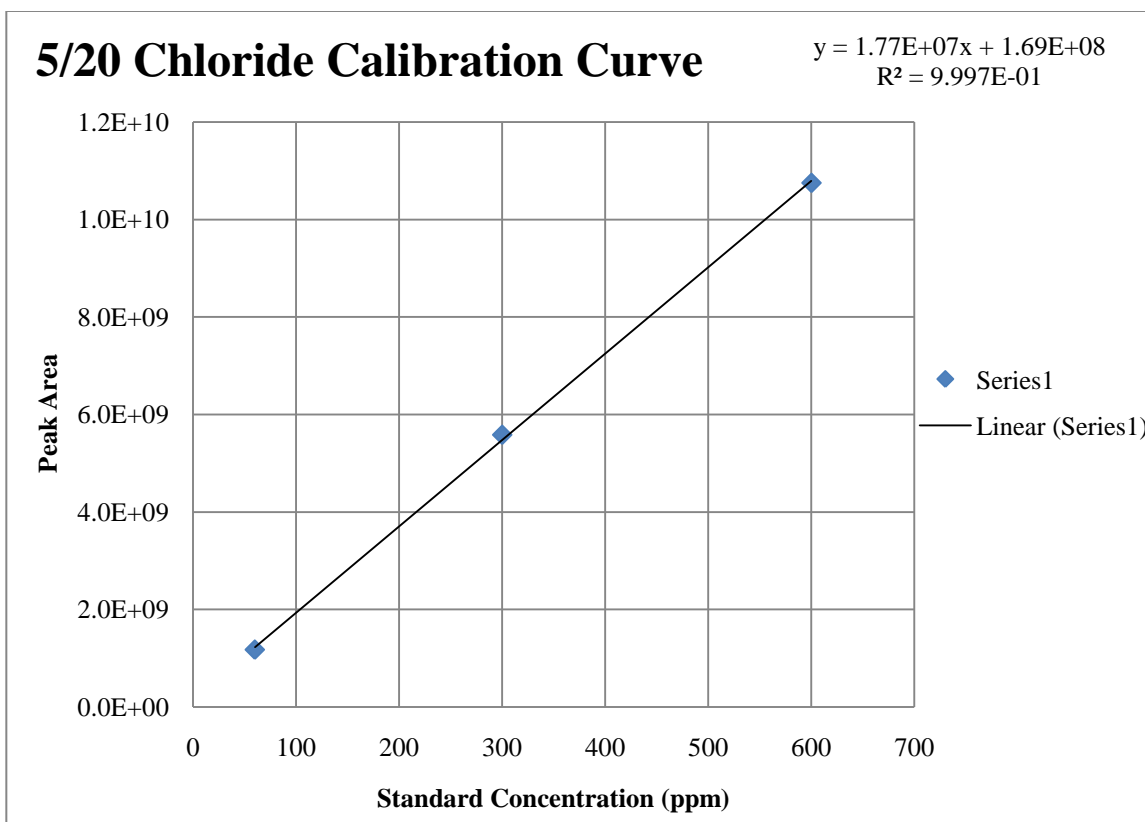


Figure 3-10: Sample Chloride Calibration Curve. Similar Curves Were Used to Determine the Concentration of Chloride, Nitrate, and Sulfate in All Samples

The data points are represented by a linear trendline with a $y = mx + b$ format. Based on the standard concentrations and the area under the curve, the trendline equation could be solved to calculate the concentration of each sample. A selected curve area is input into the equation as the y-term, thus solving for x, or the concentration in ppm. Anions were identified by selecting curve peaks at retention times determined by several iterative standard combination runs. This was done by selecting and running standard concentrations with 1-2 anions present. For example, the chloride and sulfate “only” combination standard yielded only two significant peaks. The retention time of these two peaks was recorded and used to distinguish when chloride or sulfate occurred in each sample. Nitrate followed the same technique. The resulting

retention time in order of fastest to longest was chloride, nitrate, and sulfate. This order corresponds with previous Dionex standard peak occurrences (Dionex, 2004). Each sample peak area was recorded and a corresponding concentration value was recorded.

4.0 RESULTS AND DISCUSSION

Bi-monthly samples were acquired from September 2010 to May 2011. Some data does not exist for earlier sampling months because an additional scope of work was developed during December of 2011 to include Enterococci, E. Coli, Potassium, and major anions. These parameters were chosen to expand upon data already gathered from September 2010 and to provide a better quantification of potential point and non-point sources of contamination that might exist. Shown below are **Figures 4-1 through 4-19** that point out site-site, and stream-stream variations in water quality based on pH, DO, cationic metals, anionic compounds, enterococci and E. Coli colony counts, and turbidity.

4.1 COMBINED SEWER OVERFLOW INFLUENCE

4.1.1 The Affect of CSO on pH

Natural waters typically have a pH of ~7, but urban waters like NMR often are impacted by point sources such as CSOs, illegal dumping, and other anthropogenic and natural sources. NMR has 6 CSO outfalls along its 1.8 mile above ground stretch, and one very prominent one that was sampled and referred to as sample site 1 (Collins *et al.*, 1998). A CSO from Homewood also influences NMR and joins it in the underground section upstream of the South Braddock outfall.

Sanitary sewer overflows (SSOs) also have the potential to degrade the surface water because of their substantial raw sewage input to NMR through an intersection with the Wilkinsburg culvert upstream. CSOs and SSOs can affect the pH by increasing or decreasing the acidity of the water depending on whether anaerobic or aerobic conditions exist, and how much organic matter and heavy metals are present. The pH measured at site 1 varied over time but was consistently lower than both sites up-and-downstream. The influence of the CSO on the pH in comparison to sites up and downstream of the CSO outfall is plotted in **Figure 4-1**. Bi-monthly pH readings were taken in the field from September 2010 through May 2011. The downstream site 2 had lower values or similar values than the upstream site 3 for all sample dates where low flow occurred. The sampling dates of 12/10/2010, 1/9/11, 2/4/2011, 4/11/11, and 5/9/11 were all low precipitation events. “Low flow” was determined to be when there was no precipitation in the prior 24-48 hours before a sampling, and no runoff was received through melt waters. Three sampling dates where upstream site 3 had a lower pH than downstream site 2 were during high flow events in which as much as 1 to 3 inches of rain fell in a 36-hour period (11/5/10, 3/10/11, and 5/16/11). An intermittent shower was the precipitation event during sampling on 11/5/11, resulting in a short-duration muddy flow. During conditions on 3/10/11, heavy rain and flooding occurred during sampling, while a steady rain was encountered on 5/16/11 causing higher, but clear conditions. During these precipitation events, the pH remained fairly constant between the three sites, which could be attributed to influence of the Homewood CSO, Edgewood SSOs, and Swissvale SSO that contribute flow upstream. Fluctuations did not occur because the large volume of fast moving water mitigated any potential variation of pH between sites. The pH values for these high flow events were lower than most of the pH values at low flow events.

This may be attributed to the low pH of the precipitation in the Pittsburgh area due to years of industrial applications.

The CSO outfall decreased the pH of the downstream site in NMR by 0.25-3%. Over the course of the sampling, the pH of the CSO varied between 6.8 – 7.9, while the up and downstream sites ranged from 7.3 – 9.0, and never fell below 7.3. The results show that the CSO outfall at site 1 had a lower pH than other NMR sites. Future work could include a sampling site upstream on NMR, directly below South Braddock Avenue to show pH variation between CSO outfalls along NMR.

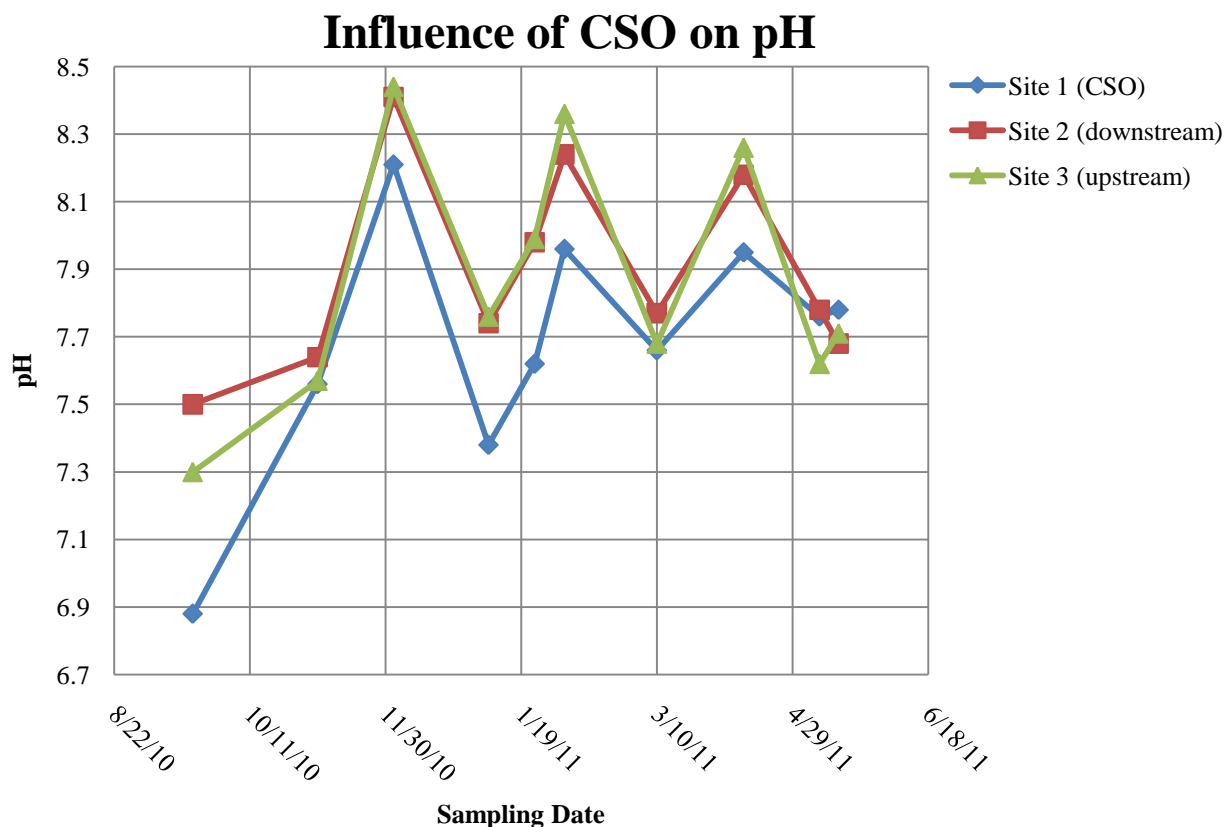


Figure 4-1: Field Measurements of pH at site 1 (CSO), site 2 (downstream of CSO), and site 3 (upstream of CSO) on NMR. The CSO consistently had a lower pH than other NMR sites throughout the study.

The pH of each tributary was also measured; the pH values for NMR, Fern Hollow, and Falls Ravine are plotted in **Figure 4-2**. NMR had the highest average pH values over the course of the study followed by Fern Hollow and Falls Ravine. Falls Ravine averaged a pH of 7.4, but most data points occurred below 7.5, which was closest to the reported 7.4 pH value of the receiving Monongahela River during monthly sampling intervals 11/08 – 12/10 at the USGS Braddock site (USGS, 2011).

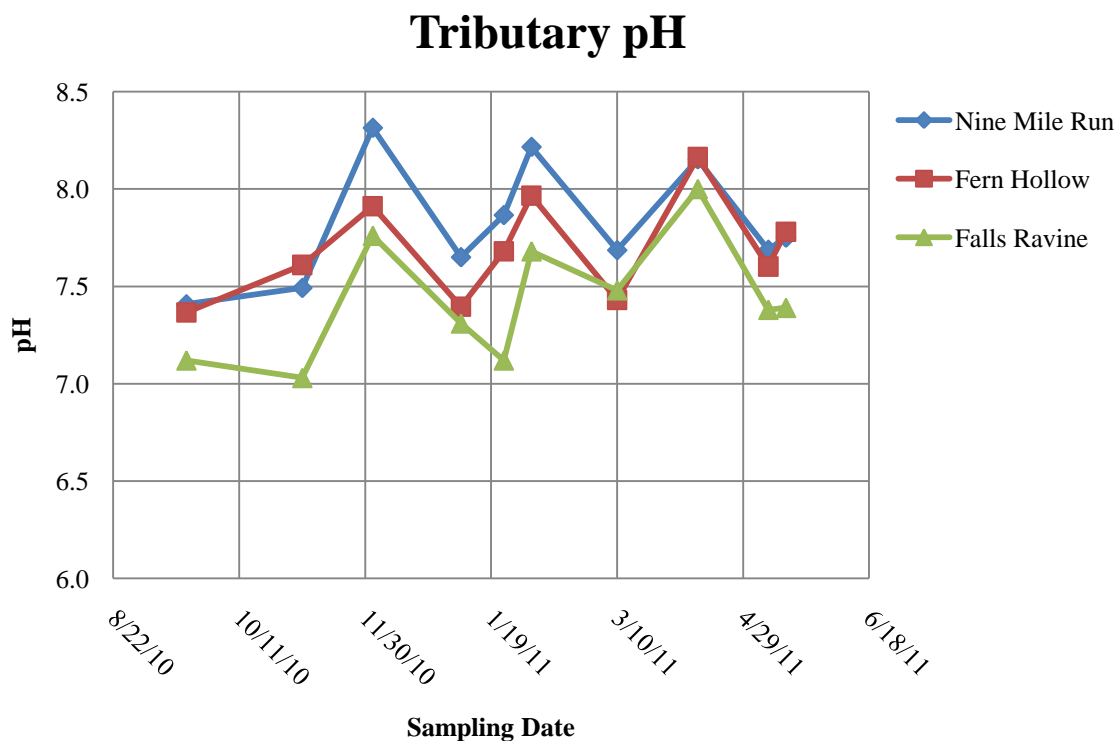


Figure 4-2: Average pH for in NMR, Fern Hollow, and Falls Ravine for each month of the study. Falls ravine had the lowest average pH of the study, while NMR consistently had the highest values between 7.5 and 8.4.

4.1.2 Dissolved Oxygen Concentration in Frick Park Streams and the CSO

Dissolved oxygen is an important parameter to quantify because it is essential to animals, fish, macrophytes, and other aquatic organisms. The ability of a stream to sustain aquatic life may be compromised if low concentrations of oxygen (<5-6 mg/L) exist in the water. Dissolved oxygen is lost to respiration and aerobic decomposition, which is a concern in the NMR watershed because of the influx of organic matter from urban runoff, leaves, and CSO seepage. Normally, dissolved oxygen concentrations increase in winter months because the colder water has the ability to hold more oxygen than warmer water. As water becomes warmer water it is more readily saturated with oxygen and therefore is less soluble in terms of DO. The highest DO concentrations can occur at 4 °C, prior to freezing.

In addition to influencing the pH, the CSO also affected the DO concentration of surrounding sites because DO is used in aerobic degradation of organic compounds that commonly exist in outflow. Field measurement results for DO at the CSO outfall site, upstream, and downstream sites are shown in **Figure 4-3**.

Data indicates that DO concentrations of the CSO are from 2-72% lower than the upstream and downstream sites and may be attributed to increased amounts of organic matter, solids, and other constituents present in sanitary sewage.

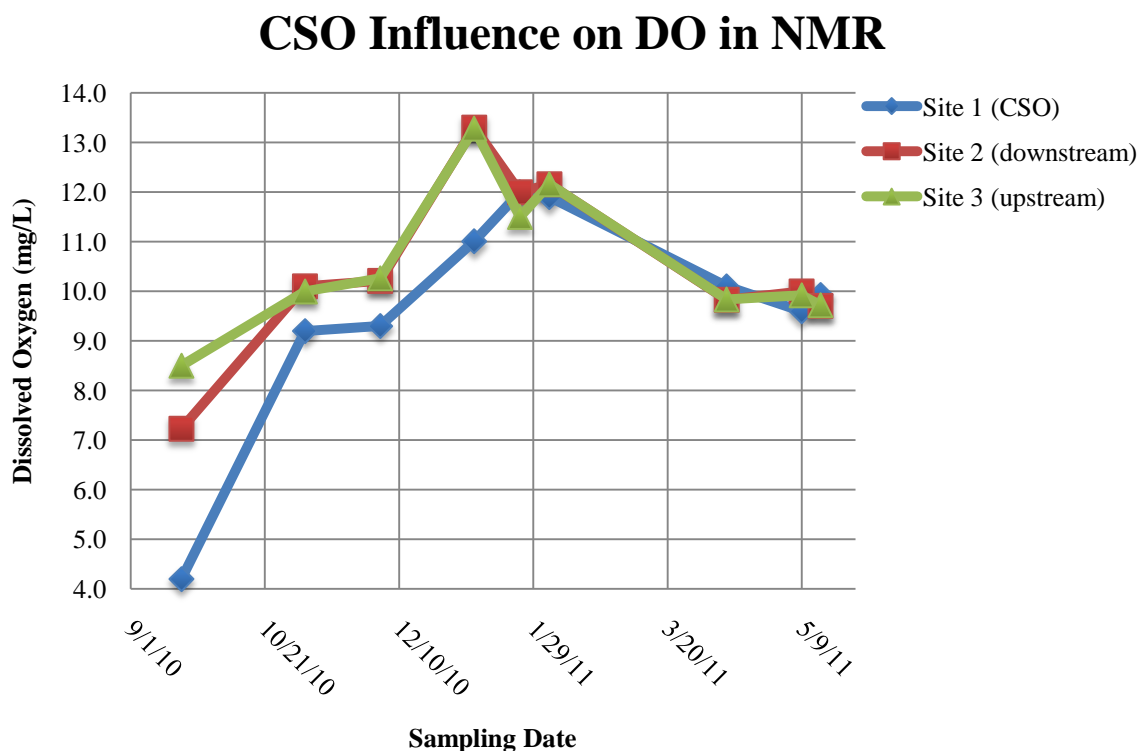


Figure 4-3: DO values for Site 1 (CSO), Site 2 (downstream), and Site 3 (upstream) of NMR displaying the low DO characteristics present at the CSO outfall.

More DO respiration is required by microorganisms present in water during degradation of these constituents, therefore resulting in a lower DO value for the CSO site. However, there was no measureable reduction of DO between the up and downstream sites in the field data.

The highest DO values occurred during January and February when the ambient temperatures were lowest. The higher DO values coincide with the colder months since cold water has the ability to hold more oxygen than warmer water. A peak in DO concentration is shown in **Figure 4-4**. The average DO value for NMR during January and February was 12.4

mg/L, while FH and FR were both 11.2 mg/L. During the months of September-December and March-May averaged DO values of 9.6, 9.5, and 8.2 mg/L for NMR, FH, and FR. Therefore, the colder months produced DO concentrations that were 29.0% higher for NMR, 18.0% for FH, and 36.0% higher in FR. Average DO concentrations for the entire sampling period resulted in values of 10.5, 10.0, and 9.2 mg/L for NMR, FH, and FR, respectively. This variability exists between streams because work has been done over the past 10 years by the USACOE on NMR to improve flow via large stone blocks. The addition of these blocks can introduce oxygen when the water of NMR circulates overtop of the block. However, all stream DO values were lower than the average DO value of 11.2 mg/L for the Monongahela River USGS Braddock Site from 11/08 – 12/10 (USGS, 2010). The NMR average was 10% lower, while FH and FR were 11% and 22% lower, respectively. Low DO concentrations feeding downstream sections of NMR could cause slight production impairment to the 14 species of fish that exist in the first 0.3 km of NMR (Koryak *et al.*, 2001b). Also, the DO values of NMR and its tributaries are of concern because of their potential impairment in the ability to meet the chemical and biological oxygen demand downstream before intersecting the Monongahela River.

Dissolved Oxygen in Frick Park Streams

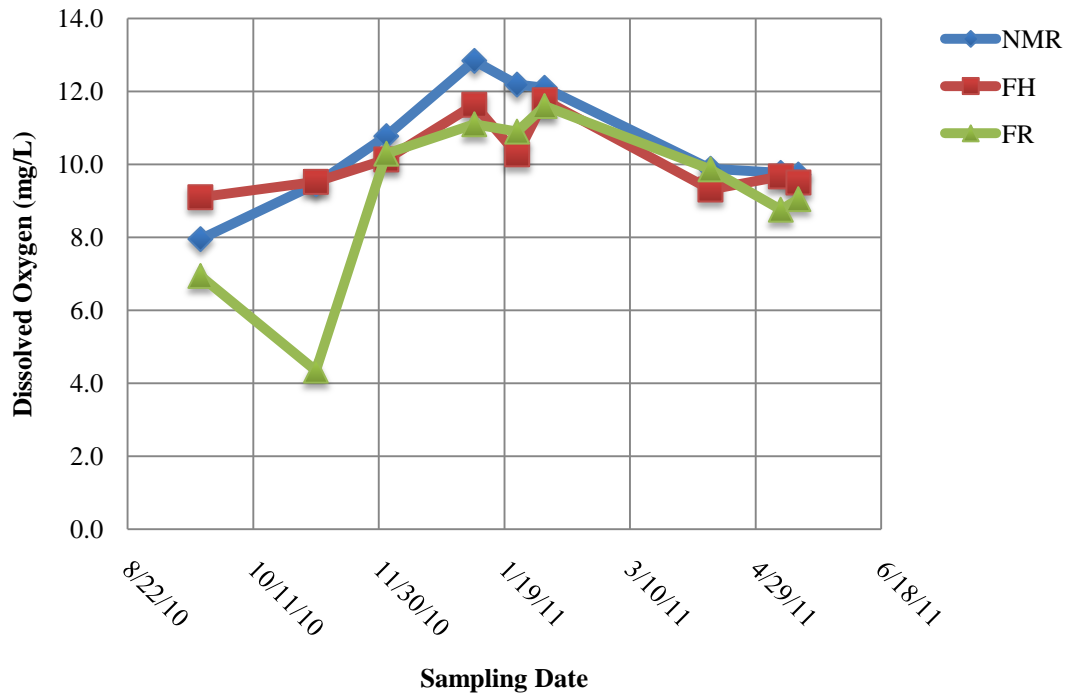


Figure 4-4: Dissolved Oxygen Concentrations in NMR, Fern Hollow, and Falls Ravine Over Entire Sampling Period (9/10 – 5/11). NMR averaged the highest DO concentrations throughout the study, with high points occurring during winter months.

4.2 METAL CONCENTRATIONS

Cationic sodium, calcium, magnesium, and potassium were measured in the lab using the atomic absorption spectrophotometer for each sampling site. Their results are plotted in **Figures 4-5 through 4-8** for each stream within Frick Park (Nine Mile Run, Fern Hollow, and Falls Ravine). Monthly concentration values were averaged for the sites that make up each stream within Frick Park. For example, sites 1-5 were averaged for NMR, sites 6, 8-12 were averaged for Fern Hollow, and site 7 represented the Falls Ravine.

4.2.1 Sodium

High sodium concentrations associated with the application of deicing agents, such as NaCl have the potential to adversely affect plants and soil surrounding a receiving body of water. Once in a stream, sodium can infiltrate the soil and adjacent groundwater. Plant growth can therefore be inhibited by the presence of sodium and the osmotic interference created during uptake of water by the roots (Munck *et al.*, 2010). This poses a threat to plants and other riparian vegetation that line the entire above ground section of NMR.

While the concentrations of sodium fluctuated throughout the duration of the observation period, NMR consistently reported the highest sodium concentration values. The NMR concentration values were, on average, 2.3x higher than values from Fern Hollow, and 3x higher than Falls Ravine sites. A plot of sodium concentration is shown in **Figure 4-5**.

Sodium Concentrations

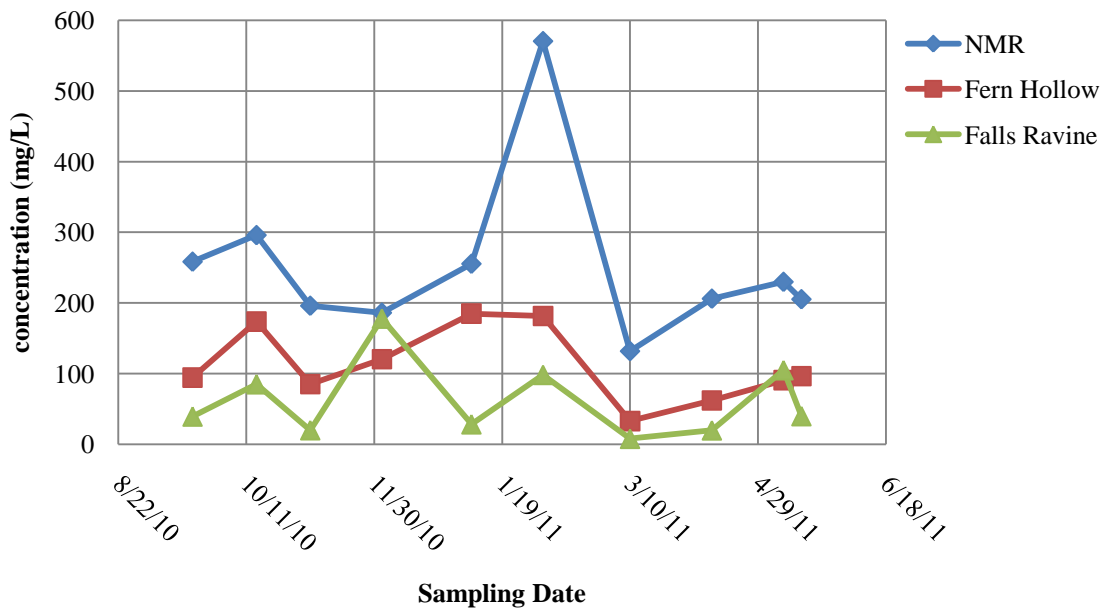


Figure 4-5: Sodium Concentration for in NMR, Fern Hollow, and Falls Ravine throughout the study. NMR exceeds other tributaries during every sampling period causing potential impairment to downstream biota.

Each sampling date was plotted separately to shown variations between stream conditions. Overall, sites 1-5 on NMR produced the highest values of Na^+ , with Fern Hollow and Falls Ravine following respectively. These highly soluble Na^+ ions are likely associated with runoff received by NMR from I-376, as well as the storm sewers that contribute flow from adjacent neighborhood roads. There was a spike in sodium content that was observed during February 2011 when 14.1 inches of snow fell on the heels of 24.1 inches of snowfall during January 2011. The large amounts of snow during these two periods correlates to the high salt load spread on the roadways during this time. A lack of precipitation during this time-period could have caused a buildup of sodium concentrations in the streams. This buildup further compounded the issue because of very low flow present during this sampling interval. The lack of precipitation would

reduce sodium from runoff, but it would not help to dilute or wash out the already high levels of previously applied road. A high precipitation event (1-3 inches in previous 36-hr), like the one observed during sampling on 3/10/11 created a much-needed washout of the system, causing the sodium levels to drop. Since the surrounding areas are highly urbanized, a high precipitation event, like the one on 3/10/11, caused extremely turbulent and flood conditions resulting in a dilution of road salt that had not been absorbed into the soil. Under these flood conditions, the lowest overall sodium concentrations were observed in all three streams. High sodium concentrations remaining from the February sampling period were diluted and/or partially washed-out during this event. Sodium concentrations for the February and March 2011 samplings are plotted on **Figure 4-6**. A plot of the two months shows the magnitude of difference that existed between the sodium concentrations of a high snowfall period and a flood event.

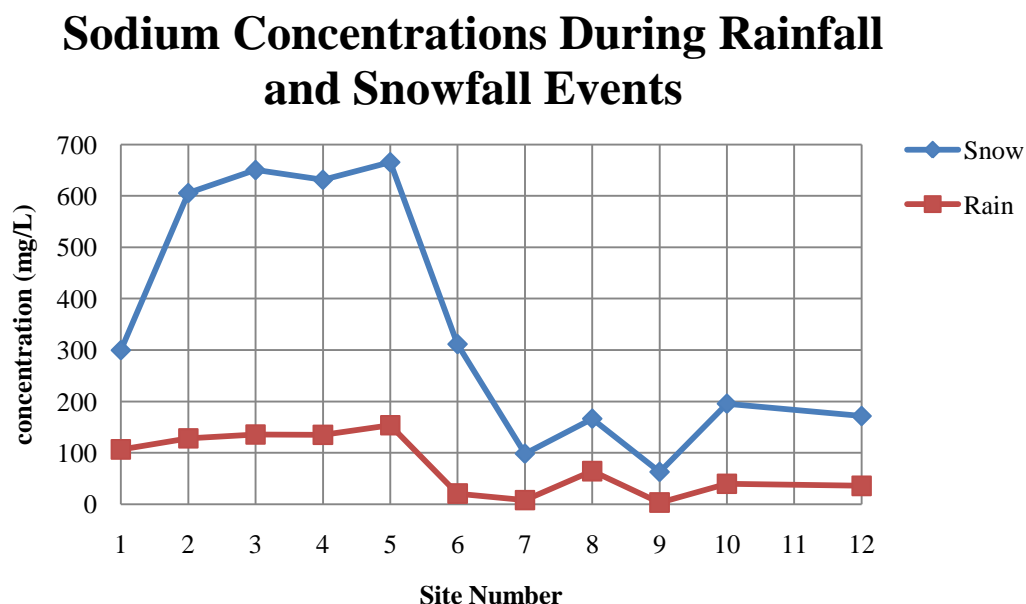


Figure 4-6: Sodium Concentrations (mg/L) During a High Snowfall Period (2/4/11) and a High Rainfall Event (3/10/11). Sodium concentrations are 3-4 times higher in NMR because of road salt during high snowfall periods.

NMR sites 2-5 always yielded the highest concentrations of sodium, while sites 7 and 9 had the lowest. The low concentrations of sodium at sites 7 and 9 would be attributed to both sites having a spring-fed or un-impaired groundwater source, and not lying next to any major roadways that would cause a spike in sodium concentration. Sites 6 and 8 were usually higher than other Fern Hollow sites due to the proximity to a park road and the Forbes Bridge, respectively. Data corresponding to **Figure 4-6** is shown in **Table 4-1**. On average, NMR sites were between 3-4 times higher during the snowy month of February, than in March. Between these months, an extremely large spike in sodium concentration occurred at sites 6 and 9. The 14x jump at site 6 can be fully attributed to the adjacent park road bridge. Large amounts of salt were visually observed on this section of the park road and bridge during the 2/4/2011 sampling. Although **Table 4-1** displays the two concentration extremes, the shock loading of using NaCl as a deicing agent during the winter months was readily observed.

Table 4-1: Site Specific Sodium Concentration Values and % Differences for 2/4/2011 and 3/10/2011. Table shows 2.5 – 14x increases in sodium concentration especially between sites 6 and 9 that reside within wooded areas of the Park.

Site Number	2/4/2011 (ppm)	3/10/2011 (ppm)	% Difference
1	300	107	181%
2	606	128	373%
3	650	135	380%
4	631	135	368%
5	666	153	334%
6	311	20.6	1410%
7	98.0	7.81	1160%
8	166	64.3	159%
9	62.6	3.20	1850%
10	196	39.8	391%
12	171	35.6	381%

4.2.2 Divalent Cations

Calcium and magnesium levels are the main contributors to water hardness. If high concentrations of Ca^{2+} and Mg^{2+} ions are present in a water source, the water is considered to be hard. Industrial applications affected by water hardness due to fouling issues include pipes, heat exchangers, and other machinery that are water-cooled. Sources of these divalent cations are found in underlying strata like limestone, as well as crushed limestone used on walking trails within Frick Park. As stated previously, the bedrock in the NMR Watershed consists of horizontal layers of shale, sandstone, claystone, limestone, and coal.

Since limestone composes a portion of the subsurface strata and is used on the walking trails, the slightly acidic rain can weather the limestone, thus releasing ions including Ca^{2+} and Mg^{2+} . In addition, PennDOT readily used sodium, calcium and magnesium salts as deicing agents in this area when the temperature dropped below $-6.7\text{ }^{\circ}\text{C}$ (PennDOT, 2010b). In the liquid slurry form, CaCl_2 and MgCl_2 are used to pretreat the roads before rock salt application at low temperatures (PennDOT, 2010b). Therefore, the concentrations of Ca^{2+} and Mg^{2+} are affected by the underlying stratigraphy, as well as the application of deicing agents during winter months.

4.2.2.1 Calcium Calcium concentrations observed in the three Frick Park streams are plotted in Figure 4-7. Fern Hollow had the highest concentrations of calcium throughout the study with an average of 120 mg/L, which was 13 % and 66% higher than NMR and Falls Ravine, respectively. Fern Hollow sites were adjacent to a park road and beneath the Forbes Bridge. The highest calcium concentrations occurred during the December 2010 sampling and correspond to the first observed usage of deicing agents during the sampling period. A

maximum of 270 mg/L for Fern Hollow, and 210 mg/L for NMR occurred during the 12/3/10 sampling date. However, the maximum calcium concentration for Falls Ravine was on 5/9/11 with a value of 200 mg/L. The lowest values of calcium coincide with the high precipitation event that occurred on 3/10/2011, and it is possible that the flooding triggered by the 1-3 inches of rainfall caused a reduction of calcium concentration that might have been in the system. However, April and May of 2011 were two of the rainiest months of the current year for Pittsburgh with precipitation totals of 5.1 inches and 4.6 inches, respectively (NOAA, 2011). Additionally, the largest 24-hour precipitation event in May 2011 occurred one day prior to the 5/16 sampling, totaling 0.97 inches (NOAA, 2011). Between April and May 2011, calcium concentrations averaged between 93.0 and 142 mg/L, which were 2-3 times higher than the monthly average of 32.0 mg/L at the Braddock site on the Monongahela River (USGS, 2011). Besides 12/3/10, April and May averaged the highest calcium concentrations.

Calcium Concentrations

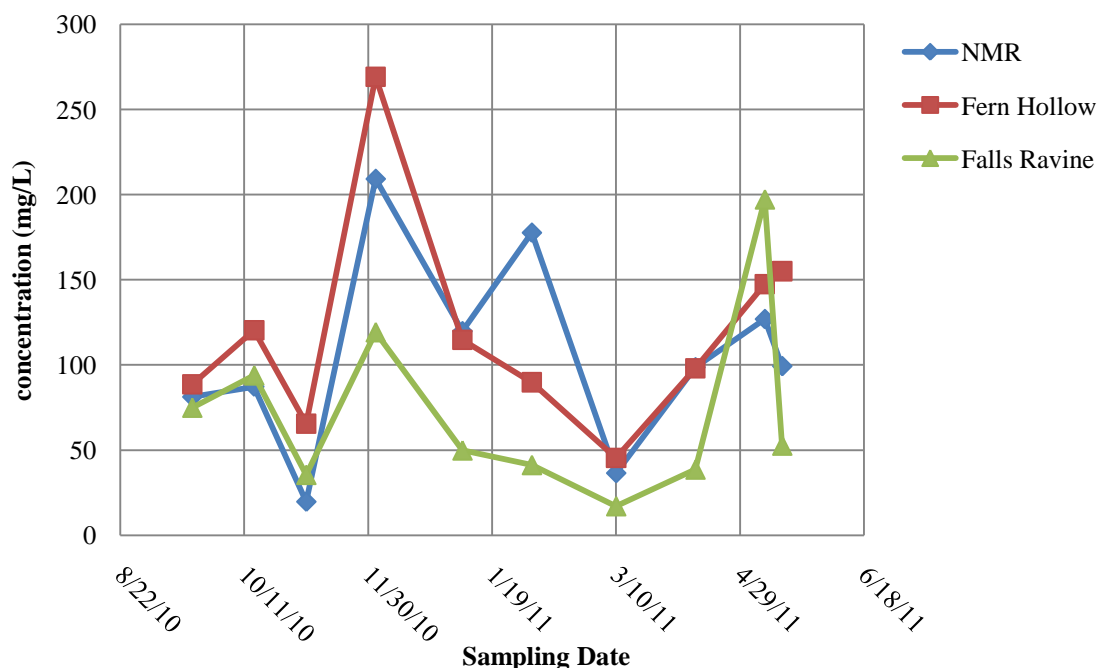


Figure 4-7: Monthly Calcium Concentrations From 9/20/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. Fern Hollow had highest calcium concentrations throughout the study, with peaks occurring during the winter months.

4.2.2.2 Magnesium Like calcium, magnesium is sourced from subsurface strata such as gypsum, dolomite, or limestone, as well as the application of $MgCl_2$, which is commonly used as a deicing agent by PennDOT.

A plot of magnesium concentration for three Frick Park streams is shown in **Figure 4-8**. Magnesium did not follow deicing related trends that were observed for calcium and sodium. The highest magnesium concentrations for all three streams occurred on the 11/5/10 sampling date, which occurred during a rain event when the temperature was 4-6 °C. Like the calcium concentrations, magnesium values were highest throughout the study for the Fern Hollow sites, followed by NMR and Falls Ravine. Average magnesium concentrations over the observation

period for Fern Hollow, NMR, and Falls Ravine were 67.0 mg/L, 44.0 mg/L, and 33.0 mg/L, respectively. The occurrence of high and low levels of magnesium did not follow a precipitation or temperature pattern like that of calcium or sodium. However, the consistently wet months of April and May 2011 yielded average magnesium values between 55.0 and 80.0 mg/L.

The magnesium concentrations did not follow the same deicing agent usage pattern as calcium. Magnesium concentrations were highest in November 2010 and May 2011, suggesting that magnesium concentrations may have been the result of natural sources instead of deicing agents. Additionally, a salt premix is commonly used in the form of 80% NaCl and 20% CaCl_2 to treat roadways (Ostendorf et al., 2006). Therefore, calcium concentrations would correspond to deicing agent usage more so than magnesium.

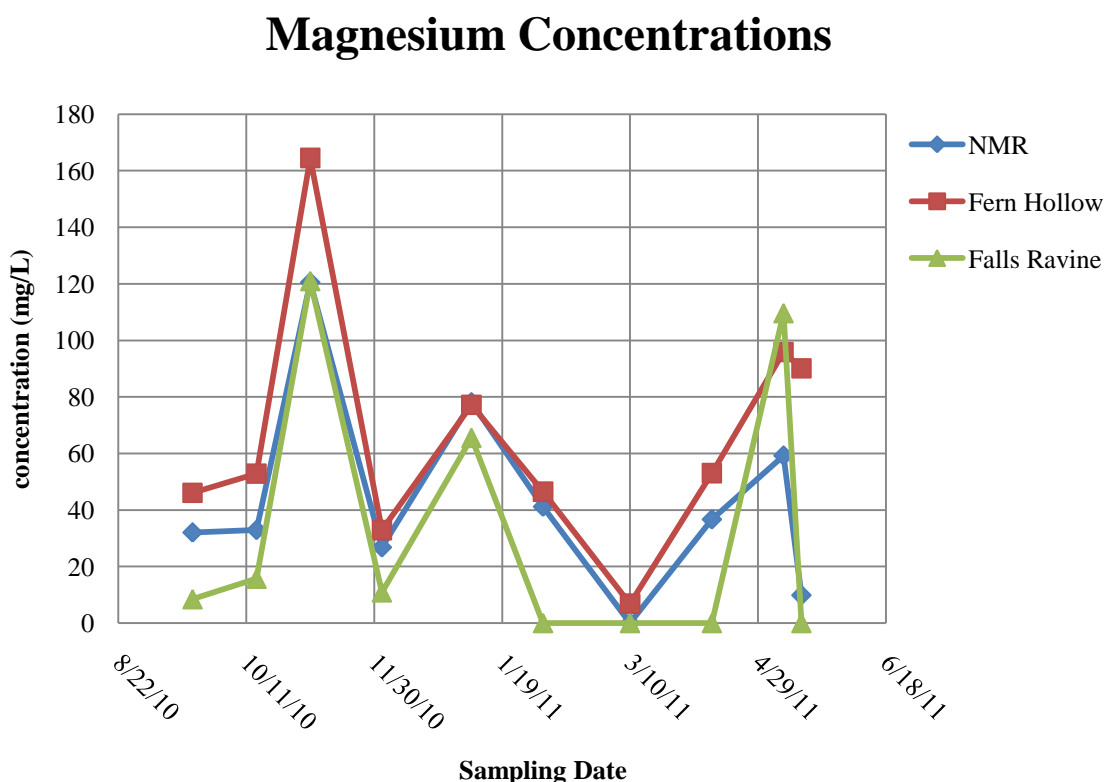


Figure 4-8: Monthly Magnesium Concentrations From 9/20/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. Fern Hollow produced the highest average Magnesium concentrations throughout the study. Seasonal patterns did not follow deicing agent usage, but rather showed higher concentrations during warmer months.

4.2.3 Potassium

Potassium is a necessary ion used in synthetic fertilizers and at elevated quantities, may have adverse environmental and health effects. Potassium is a dietary requirement for almost every organism and is critical for nerve function (Lenntech, 1998-2009). Potassium releases are often associated with dead plant and animal material, and can be adsorbed to clay minerals prior to being dissolved in water. It is commonly used in synthetic fertilizer in the form of potassium nitrate, and is usually found in clays and fine sediments (Lenntech, 1998-2009).

Although not very hazardous in water, concentrations increase rapidly due to its high mobility and low transformation potential (Lenntech, 1998-2009). Where magnesium and calcium have little to no health effects, high levels of potassium are associated with adverse health effects that are usually due to the other components potassium is commonly compounded with. Excessive skin contact to potassium metals can cause severe irritation, especially the eyes, and when combined with chloride and nitrate can have additional health effects (Lenntech, 1998-2009).

Fern Hollow yielded the highest average potassium concentration of 4.2 mg/L, while Falls Ravine had the lowest average of 2.5 mg/L. Potassium concentrations for the three Frick Park streams are plotted in **Figure 4-9**. Measurements were generated for a time period between 12/3/10 through 4/11/11. Values remained consistent through the time period with the exception of measurements done on 3/10/11. The high precipitation event on this day could be the cause of the substantially low readings in each stream. Potassium is water soluble and high precipitation events like 3/10/11 could have caused the washout as was seen for calcium, sodium, and magnesium. For example, 3/10/11 K values on NMR were 2.6 times lower than the average concentration value of 4.1 mg/L, while Fern Hollow and Falls Ravine saw a 1.75x and 2.1x

reduction, respectively. The CSO produced the highest value of the sampling period (6.7 mg/L), and consistently averaged the highest concentrations of any site (4.4 mg/L). This could be a result of the effluent of the CSO containing a high potassium load associated with household detergents and soaps. Concentration values for potassium were not observed to fluctuate with seasonal variations, but the high flow event on 3/10/11 diluted the potassium. The potassium concentrations for all Frick Park tributaries ranged between 1.2-6.7 mg/L (avg. = 4.0 mg/L), which is 2 times higher than the average value of 1.9 mg/L observed at the USGS Braddock Site on the Monongahela River from 11/90 – 9/04 (USGS, 2011).

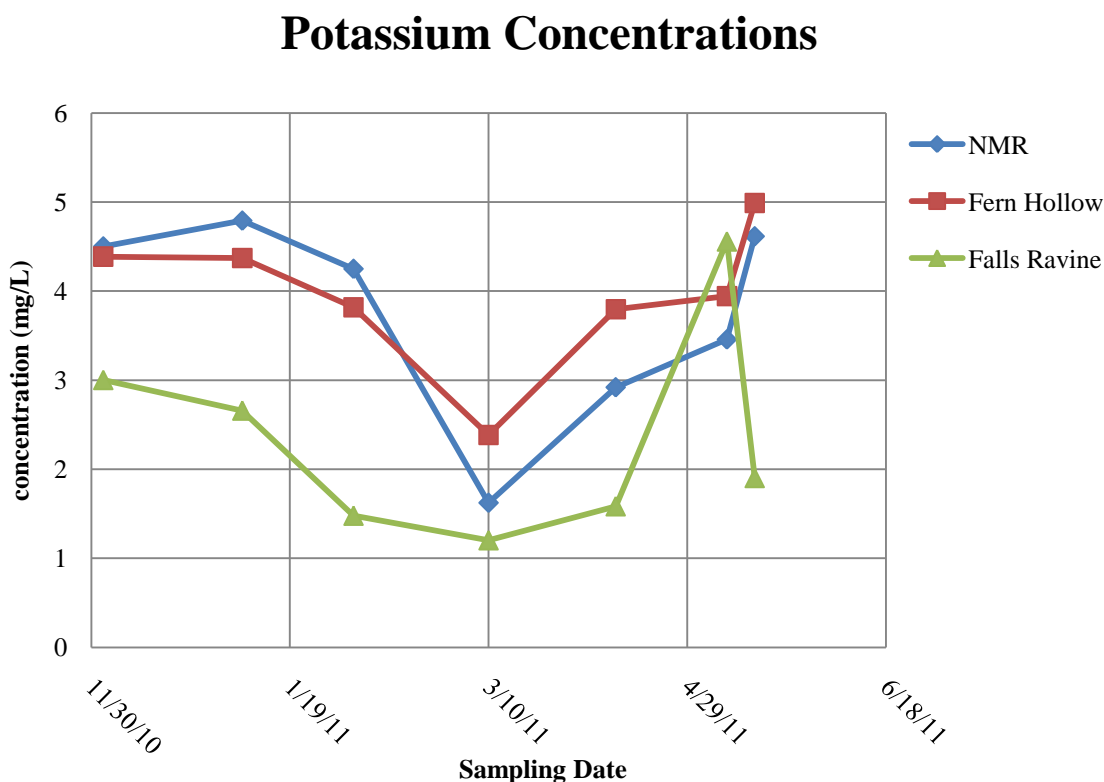


Figure 4-9: Monthly Potassium Concentrations From 12/3/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. Fern Hollow consistently yielded the highest potassium concentrations throughout the study.

4.3 MAJOR ANIONS (NO_3^- , SO_4^{2-} , Cl^-)

Anion concentrations were evaluated for nitrate (NO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-). Nitrates and sulfates were measured using the Ion Chromatograph (IC), while chloride was measured using both the IC and chloride ion selective electrode (ISE). Chloride concentrations as high as 2400 mg/L were measured on the IC causing the chloride peak to overlap that of the phosphate (PO_4^{3-}) ion, masking phosphate quantification. Therefore the IC did not readily detect phosphate in the presence of such high chloride content. In addition, when standard phosphate solutions were tested, undetectable levels of phosphate were observed in the peaks of the IC. This was attributed to the fact that phosphate is usually present at low concentrations in surface waters. The IC results were masked by chloride and standard solutions yielded non-detectable results, so phosphate levels were not analyzed.

4.3.1 Chloride

Chloride concentration is an excellent indicator of deicing agent contamination because its conservative presence in surface and groundwater (Ostendorf *et al.* 2006). In addition to deicing agents, natural sources of chloride include rock-water interactions, saline seeps, or minor atmospheric contributions (Kelly *et al.*, 2010).

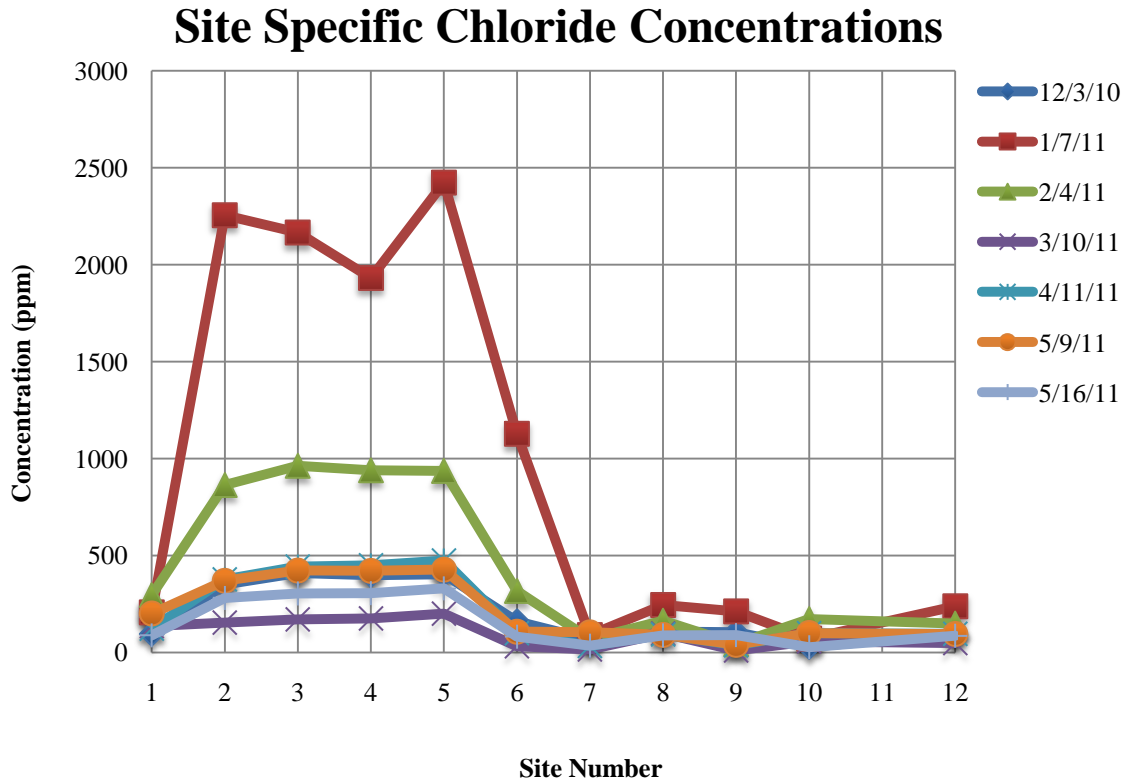


Figure 4-10: Monthly Chloride Concentrations From 12/3/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. High snowfall periods 1/7/11 and 2/4/11 yielded the highest chloride concentrations of the sampling period.

Chloride is commonly paired with calcium, sodium, or magnesium in deicing agents, and as a result, chloride concentrations were especially high during the winter months. Chloride concentrations were measured from 12/3/10 through 5/16/11, the results are shown in **Figure 4-10** for chloride concentrations at each sampling site. Concentration values as high as 2430 mg/L occurred at site 5 on NMR during the 1/7/11 sampling period in which 24.1 inch of snow fell that month. High values of 1130 mg/L, 1930 mg/L, 2170 mg/L, and 2260 mg/L were observed during this sampling period at sites 6, 4, 3, and 2, respectively. These values were approximately 2-3.5 times higher the next highest values that occurred on 2/4/2011. Sites 2-5 are on NMR, while site 6 (on Fern Hollow) is directly adjacent to a park road. All of these areas saw a high salt load during the months of January and February. The high chloride

concentrations correspond to the wintery conditions that were present in the month of January. January was the coldest month, with 1.8 inches of snow falling in the 24 hours prior to sampling. The cold temperatures, along with the snowfall caused a large increase in deicing agents such as, rock salt and salt brine application along the I-376 corridor and neighborhoods adjacent to NMR. In addition, it should be noted that during the 1/7/11 sampling, sites 8 and 12 averaged 240 mg/L, while the more isolated site 10 was 2.4 times less with a concentration of 70 mg/L. This difference would be the result of deicing runoff from the overlying Forbes Bridge above site 8. It is no coincidence that the highest levels of chloride occurred in the two snowiest months of the winter, suggesting deicing agent contamination. While January and February showed the highest chloride concentrations in all tributaries, the preceding and subsequent months did not yield values higher than 103 mg/L on Fern Hollow and Falls Ravine. Again, the lowest concentrations ensued during the high flow event of 3/10/2011 causing a dilution of any chloride present at the time and resulting in chloride concentrations as low as 14 mg/L.

To further compare tributary specific differences, stream specific chloride concentrations were plotted in **Figure 4-11**. The CSO was separated from NMR in this case because source water flowing from the CSO outfall is not from NMR. NMR displayed the highest average chloride values (690 mg/L) at every sampling throughout the study, especially in January and February. When average NMR chloride concentrations were compared to USGS monthly chloride data at the Braddock site from 12/09 – 5/10, NMR exceeded the 42.0 mg/L USGS average by over 15 times (USGS, 2011). Levels of chloride as low as 210 mg/L have been shown to impair land, aquatic plants, and aquatic invertebrates of surface waters, creating the possibility for the degradation of downstream sites on NMR (Kelly *et al.*, 2010).

Disregarding the high values in each tributary for January and February, NMR still, by far, had the highest chloride concentrations over the study period. An average of 340 mg/L was recorded for NMR, while the CSO, Fern Hollow, and Falls Ravine sites all yielded values of 130 mg/L, 79 mg/L, and 50 mg/L, respectively.

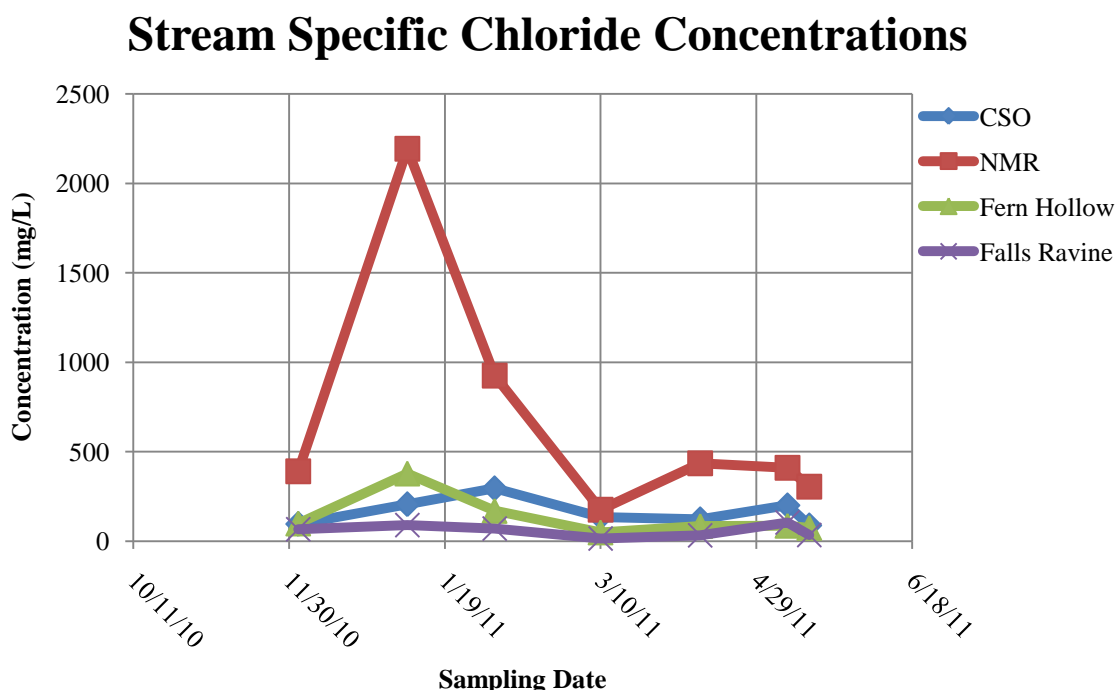


Figure 4-11: Frick Park Stream Chloride Concentrations Over Duration of 12/3/2010 – 5/16/2011. NMR possessed the highest chloride concentrations throughout the study, especially in the winter months.

4.3.2 Nitrate

Nitrates are a nitrogen-oxygen negatively charged chemical unit that can combine with various organic and inorganic compounds. It is primarily used as a fertilizer, and once taken into the body, it is converted to nitrite (USEPA, 2010a). Due to the large population of families and young children that live around and play in the waters of Frick Park, health concerns with regards to nitrate contamination exist. Infants below six months old can develop shortness of breath or a health effect called Methemoglobinemia (Blue Baby Syndrome) if they drink water

contaminated with nitrate in excess of the 10 mg/L maximum contaminant level (MCL) (USEPA, 2010a). Methemoglobinemia affects the hemoglobin found in red blood cells. It causes a buildup of hemoglobin, therefore reducing the amount of oxygen that can be carried to body tissues. Additional health risks associated with nitrate-contaminated drinking water include cancer and reproductive issues (Galloway *et al.*, 2008).

Nitrate concentrations from 12/3/10 – 5/16/11 are represented in **Figure 4-12** and suggest the potential risk for health issues due to concentrations as high as 1200 mg/L. The highest nitrate concentrations occurred during the 1/7/11 sampling. The January 2011 sampling at site 5 had a nitrate concentration of 1200 mg/L, with sites 2-6 averaging 880 mg/L. While sites 2-6 had the highest values, the remaining sites had an average of only 6.7 mg/L. The 1/7/11 sampling far exceeded values from the other sampling periods and correspond to the occurrence of the highest chloride values. This nitrate spike during 1/7/11 could be attributed to an influx of animal or human waste from contributing SSOs and CSOs that feed NMR (Bruce and McMahon, 1996). High levels of nitric acid could also have contributed to this spike in nitrate. Average nitrate concentrations from 1/7/11 were 4x higher than the next highest sampling, which was 5/9/11 with a value of 78 mg/L.

Site Specific Nitrate Concentrations

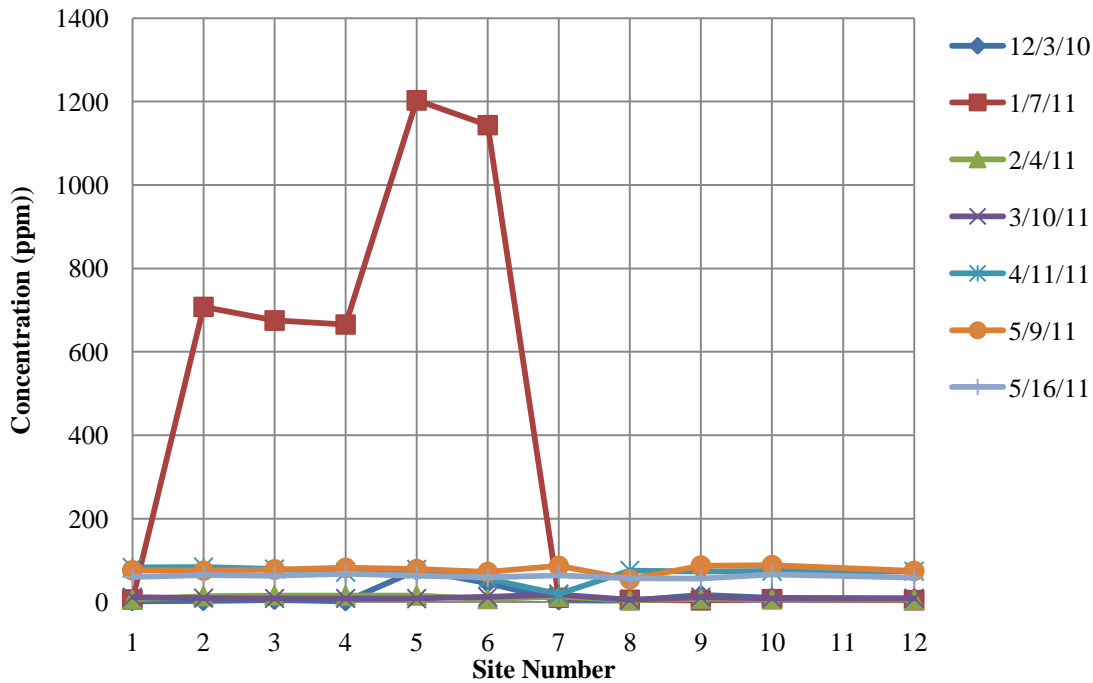


Figure 4-12: Nitrate Concentrations for Each Sampling Site from 12/3/10 – 5/16/11. Sampling on 1/7/11 yielded the highest values of Nitrate, which were 4.2 times higher than the next highest values during 5/9/11.

As stated above, the next highest sampling took place on 5/9/11, and was followed by 4/11/11 and 5/16/11. To better show the difference between samplings and improve the scale, the 1/7/11 data was removed, and the remaining sampling periods were plotted in **Figure 4-13**. With the 1/7/11 data removed, the highest nitrate values occurred during the warmer months, while December, February, and March were lowest. The April and May data also seemed to form an upper group that averaged 55-60 mg/L higher than the colder months, which may correspond to the time of year when residential lawns and gardens were being fertilized. Frequent fertilization was observed in Regent Square and surrounding neighborhoods during May 2011.

The application of fertilizer combined with the heavy rains during early May (4.58 inches) could have resulted in the 77 mg/L average nitrate concentration during this period. Heavy rains caused fertilizers to run off of lawns into storm sewers channeling flow from surrounding neighborhoods directly into NMR and its tributaries, resulting in nitrate concentrations that were 5-6.5 times higher than the MCL.

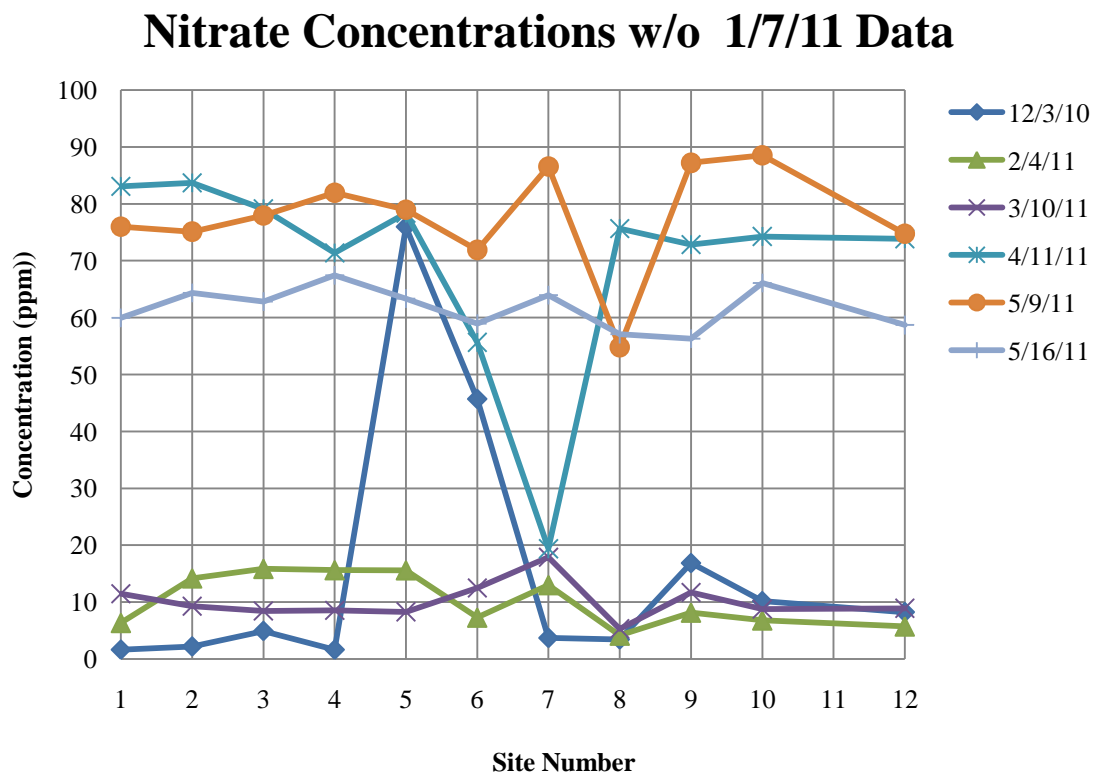


Figure 4-13: Nitrate Concentrations for Each Site without data from the 1/7/11 sampling period. The warmer months of April and May 2011 when fertilizers are typically applied had the highest nitrate concentrations.

4.3.3 Sulfate

Sulfate is naturally occurring in surface waters and currently has a secondary maximum contaminant level (SMCL) of 250 mg/L based on aesthetic effects (USEPA, 2010b). However, this is not a Federally enforceable standard, but provides a guideline for sulfates since health concerns have been raised associated with diarrhea and the ingestion of levels of sulfate that exceed the SMCL of drinking waters (USEPA, 2010b). The sulfate results followed a similar trend to that of nitrate, with the warmer months producing the highest concentrations. The 5/9/11 sampling had the highest average sulfate concentration of 260 mg/L, with a high of 420 mg/L occurring at site 7 on Falls Ravine. The warmer months of April and May defined the upper limits of the sulfate site-by-site concentrations plotted in **Figure 4-14**.

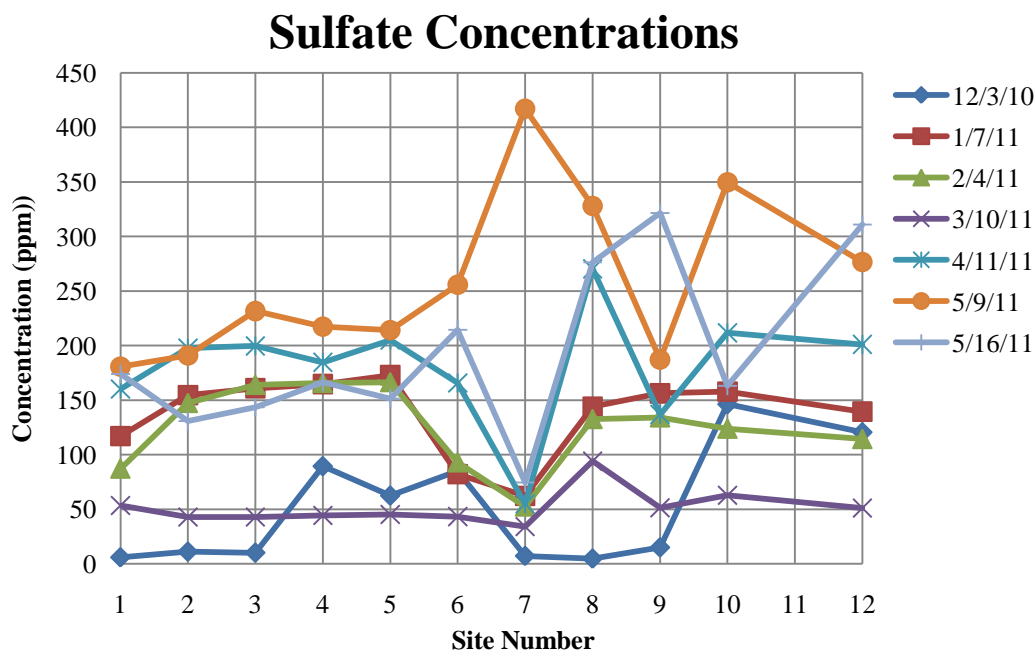


Figure 4-14: Sulfate Concentrations at each site for a sampling period of 12/3/10 – 5/16/11. The highest sulfate concentrations occurred during the 5/9/11 sampling.

A gap between the warmer and colder months in **Figure 4-14** also exists like that of the nitrate data in **Figure 4-13**, but on a smaller scale. Sulfate concentrations were fairly consistent throughout the study between sampling sites, rarely varying more than 15% between sites. However, site 7 seemed to be the exception to this.

Concentrations at site 7 were the lowest for the six other samplings, but on 5/9/11 conditions yielded the highest concentration of sulfate for the entire study. The low concentrations at site 7 during the other six samplings were expected because Falls Ravine is spring fed and travels through primarily wooded parkland. This trend was further evaluated in **Figure 4-15** by plotting sulfate concentrations in each Frick Park tributary. Falls Ravine, with the exception of 5/9/11, had the lowest sulfate concentrations of approximately 50 mg/L, followed by the CSO, Fern Hollow, and NMR, respectively. An increase in sulfate concentration was also observed during the months of April and May when comparing the Frick Park tributaries. The lowest values occurred during the 12/3/10 and 3/10/11 samplings. The 3/10/11 sampling was during a high precipitation event that could have caused a washout of any significant sulfate concentrations, resulting in the low values.

Of the seven sampling periods, only the 5/9/11 exceeded the SMCL. The 260 mg/L site average during this period was only 3.6% higher than the 250 mg/L specified by the SMCL. All other sampling periods fell below this level, allowing for the conclusion that sulfates are not a major factor in the degradation of the water quality in Frick Park.

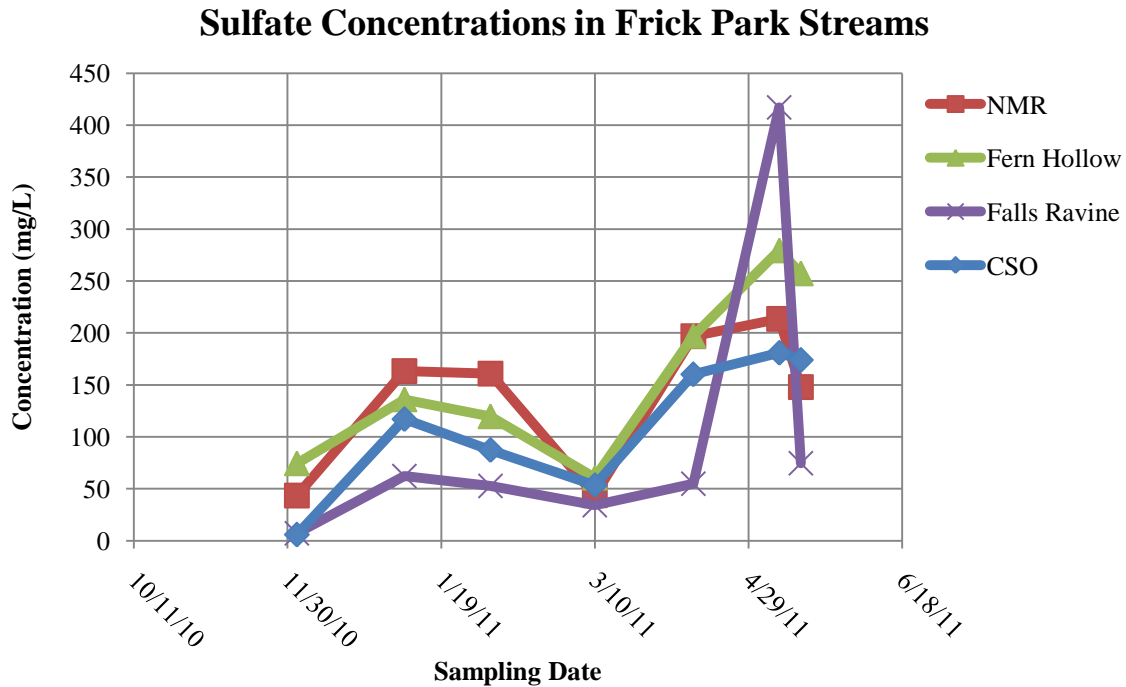


Figure 4-15: Sulfate Concentrations in NMR, Fern Hollow, and Falls Ravine between 12/3/10 – 5/16/11. Fern Hollow averaged the highest sulfate concentrations over the sampling period, but Falls Ravine had the single highest value of 417 mg/L

4.3.4 Charge Balance

A charge balance was performed for the major ions monitored throughout the study to evaluate the accuracy of the concentration values for the above cations and anions. Seven out of the nine ions below, with the exception of nitrate and phosphate, make up 90% of the dissolved solids in ground water at concentrations usually greater than 1 mg/L (Fetter, 2001). Silica (SiO_2), a nonionic species, is also typically present at concentrations greater than 1 mg/L (Fetter, 2001), but was not included in this analysis. A charge balance was performed for three dates (5/9/11, 2/4/11, and 1/7/11) on all NMR sites (sites 2-5), and is shown in

Table 4-2. The dates were selected to compare conditions present during a warmer month of May 2011, and during winter months of January and February 2011. January 2011 was also chosen so the high nitrate values observed during this period can be evaluated for accuracy. Every ion except for bi/carbonate was directly analyzed using the concentrations found during that time period. Based on the field pH values of the sampling periods, bicarbonate was selected and reported as total alkalinity. The concentrations of each measurable parameter was divided by its molecular weight (mg/mole), and then multiplied by a charge equivalence to get a total equivalent/liter. These values were summed for respective cationic and anionic species. These totals were then used to generate a charge balance error (CBE), which is shown at the bottom of

Table 4-2.

Charge balance errors for each sampling date range between 8% (5/9/11), 14% (2/4/11), and -52% (1/7/11). The 8% and 14% CBEs are near acceptable levels, but the -52% CBE is well out of an acceptable range. This large difference could be a result of other naturally occurring ions that were not included in this analysis such as, silica, iron, fluoride, strontium, aluminum, boron, nitric acid, or other inorganic/organic acids. Another source of error could be in the lab measurement of bicarbonate. By waiting until the sample is back in the lab, carbonate material can precipitate in the portion of the sample collected for anion analysis, thus removing the bicarbonate (Fetter, 2001). The large CBE difference during 1/7/11 could explain why an unusually high nitrate value (avg. 880 mg/L) for NMR was observed during this date. Either large influx of a naturally occurring substance was present in NMR during this sampling period, or a false peak was generated on the IC.

Table 4-2: Charge Balance for Cations and Anions during various conditions during sampling. Concentrations were evaluated during Spring and Winter conditions. A percent difference was calculated between the positively and negatively charges parameters for each date on NMR sites (2-5).

5/9/11 - Spring Conditions

	Conc.	Mol. Wt.	Ch. Equiv.	Ch. Eq/Liter		Conc.	Mol. Wt.	Ch. Equiv.	Ch. Eq/Liter
Cations	(mg/L)	(mg/mole)	(# ch./mole)		Anions	(mg/L)	(mg/mole)	(# ch./mole)	
Calcium	129.0	40100	2	6.43E-03	Chloride	410.0	35450	1	1.16E-02
Sodium	240.0	22990	1	1.04E-02	Sulfate	214.0	96060	2	4.46E-03
Magnesium	60.0	24300	2	4.94E-03	Nitrate	79.0	62007	1	1.27E-03
Potassium	3.0	39100	1	7.67E-05	Phosphate	10.0	94970	1.5	1.58E-04
					Bicarbonate	65.0	60010	1	1.08E-03
TOTAL				2.19E-02	TOTAL				1.85E-02
CBE				8%					

2/4/11 - Wintry Conditions

	Conc.	Mol. Wt.	Ch. Equiv.	Ch. Eq/Liter		Conc.	Mol. Wt.	Ch. Equiv.	Ch. Eq/Liter
Cations	(mg/L)	(mg/mole)	(# ch./mole)		Anions	(mg/L)	(mg/mole)	(# ch./mole)	
Calcium	194.0	40100	2	9.68E-03	Chloride	926.0	35450	1	2.61E-02
Sodium	638.0	22990	1	2.78E-02	Sulfate	161.0	96060	2	3.35E-03
Magnesium	43.0	24300	2	3.54E-03	Nitrate	15.0	62007	1	2.42E-04
Potassium	5.0	39100	1	1.28E-04	Phosphate	10.0	94970	1.5	1.58E-04
					Bicarbonate	65.0	60010	1	1.08E-03
TOTAL				4.11E-02	TOTAL				3.10E-02
CBE				14%					

1/7/11 - Wintry Conditions

	Conc.	Mol. Wt.	Ch. Equiv.	Ch. Eq/Liter		Conc.	Mol. Wt.	Ch. Equiv.	Ch. Eq/Liter
Cations	(mg/L)	(mg/mole)	(# ch./mole)		Anions	(mg/L)	(mg/mole)	(# ch./mole)	
Calcium	127.0	40100	2	6.33E-03	Chloride	2194.0	35450	1	6.19E-02
Sodium	278.0	22990	1	1.21E-02	Sulfate	163.0	96060	2	3.39E-03
Magnesium	79.0	24300	2	6.50E-03	Nitrate	813.0	62007	1	1.31E-02
Potassium	4.6	39100	1	1.18E-04	Phosphate	10.0	94970	1.5	1.58E-04
					Carbonate	65.0	60010	1	1.08E-03
TOTAL				2.50E-02	TOTAL				7.96E-02
CBE				-52%					

Charge Balance Error Calculated using the following equation:

$$CBE = \frac{\sum_{cations} - \sum_{anions}}{\sum_{cations} + \sum_{anions}} * 100$$

4.4 BACTERIAL CONTAMINATION

4.4.1 Enterococci

Enterococci were measured because they are indicator organisms for harmful pathogenic bacteria that might be present in surface waters (USEPA, 1997). **Figure 4-16** shows data for Enterococci colonies observed during the sampling period at site-specific locations. These site grouping were chosen to show the effect of the CSO on NMR, and site 12 on the remaining Fern Hollow sites. The number of colony forming units (CFU)/100 mL is shown on the y-axis while sampling date is on the x-axis (12/3/10, 2/4/11, 3/10/11, 4/11/11, 5/9/11, and 5/16/11). Colony numbers were the highest during the entire study for CSO and NMR sites (1060 and 1050 CFU/ 100 mL). This was likely due to the effluent and bacteria that flow from the CSO outfall and adjacent sanitary sewer overflow (SSO) locations that contribute to the culverted section of NMR.

Enterococci at Sites of Interest

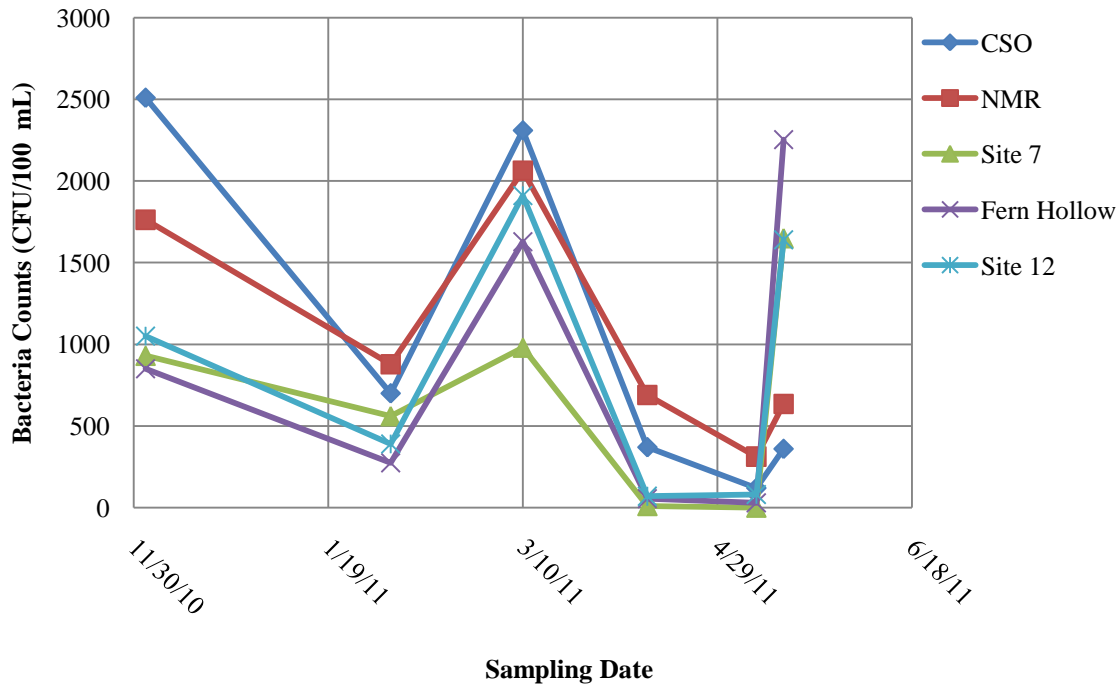


Figure 4-16: Enterococci Plate Counts at for the CSO, NMR, Site 7, Fern Hollow Sites, and Site 12. CSO and NMR had the highest number of CFU/100mL throughout the study, while site 12 consistently yielded higher colony numbers than Fern Hollow sites.

Fern Hollow and site 12 had slightly lower average concentrations of 850 and 860 CFU/100 mL, respectively when compared to NMR and the CSO. Site 12 is located on Fern Hollow, but is downstream from the Hot Dog Dam and site 8. It is significant that site 12 yielded higher counts throughout the study when compared to Fern Hollow sites because of the potential fecal matter contribution from dogs. The only exception occurred during the 5/16/2011 sampling date, which had May's highest 24-hour precipitation event (0.97 inches), the day prior. This trend is shown by **Figure 4-17**, which compares enterococci concentrations of six samplings between Fern Hollow sites and site 12. Samplings 1-6 correspond to dates between 12/3/10 – 5/16/11. Five of the six samplings resulted in higher enterococci concentrations at site

12 than in Fern Hollow. Sampling to sampling comparisons showed that site 12 had 17-27% more enterococci colonies than the other Fern Hollow sites. A maximum difference occurred on 5/9/11 in which site 12 was 170% higher than Fern Hollow. However, sampling period 6 on 5/16/11 saw a 27% concentration increase in enterococci colonies for the Fern Hollow sites.

A large volume of animal traffic was observed around Fern Hollow and in the Hot Dog Dam at all times of the year. The high values at site 12 show that the Hot Dog Dam had a great influence on the microbial concentrations of downstream Fern Hollow sites and the surrounding area. Fecal contamination due to dogs in this area of Frick Park can be considered a major public health concern.

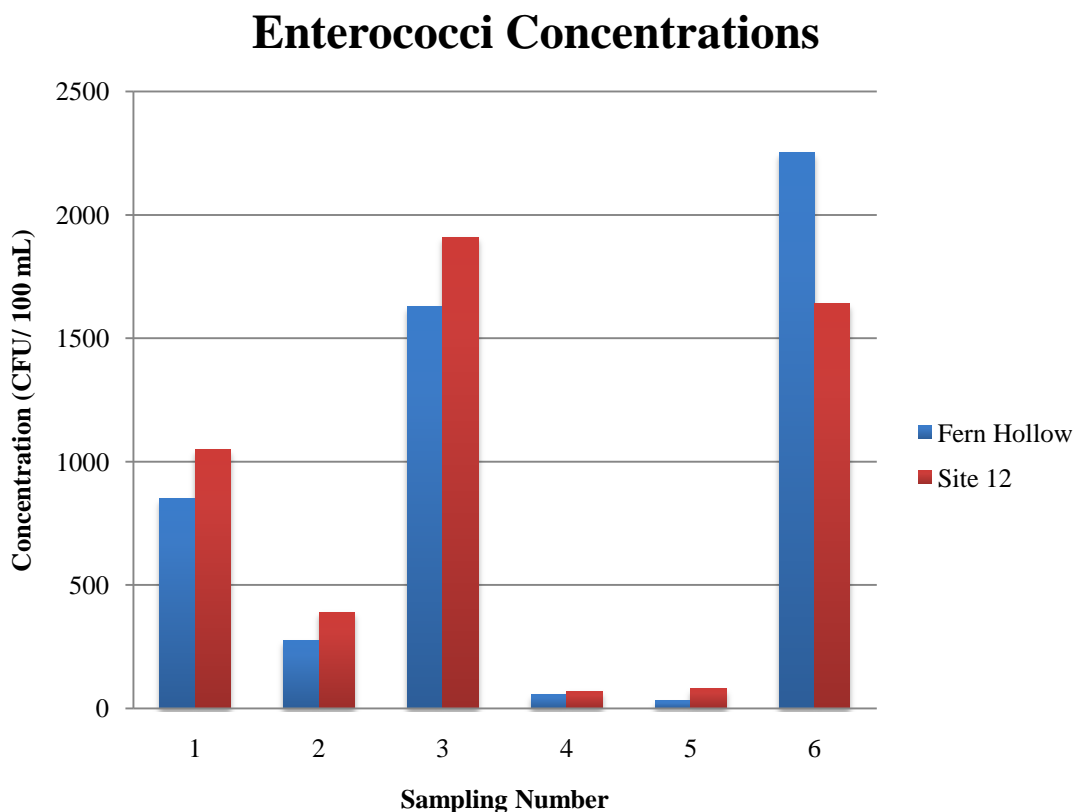


Figure 4-17: Fern Hollow vs. Site 12 Enterococci Concentrations at Six Sampling Dates (12/3/10 – 5/16/11). Site 12 had higher concentrations of enterococci at 5/6 sampling dates.

4.4.2 E. Coli

E. Coli agar was used as a medium to pinpoint which sites were contaminated with animal or human waste because they live in the digestive system of humans and other warm-blooded animals (DEQ, 2010). Other sources include illicit waste connections to storm sewers, roadside ditches, septic systems, combined sewer overflows, and sanitary sewer overflows (DEQ, 2010). The presence of E. Coli colonies indicated the potential risk for gastrointestinal illness of the surrounding communities that use Frick Park. The results of E. Coli plate counts at sites of interest are shown in **Figure 4-18**. Data in **Figure 4-18** was arranged similar to that of **Figure 4-16** to show a comparison between potential sources of contamination. The site 12 value during high flow on 3/10/11 was by-far, the highest of the study at 5800 CFU/100 mL, which resulted in a 230% increase from upstream site 8. NMR consistently produced the highest average colonies (2490 CFU/100 mL +/- 1300) of E. Coli except for the 3/10/11 sampling date when E. Coli was non-detectable. However, the 3/10/11 sampling yielded the highest enterococci counts for NMR of the study resulting in large numbers of bacteria, but not in the form of E. Coli. The next highest number of colonies occurred at site 12, in which an average of 1880 CFU/100 mL was observed over the course of the study. At NMR sites, the high levels of E. Coli were the result of the upstream sewage contribution of the Homewood CSO, the SSOs from Edgewood and Swissvale, runoff from adjacent storm sewers. On Fern Hollow, site 12 is downstream from the sites 8, 9, and 10, and follows a braided channel network through a marsh between sties. It is dense with trees and plant life, with no other contamination sources beside the upstream Hot Dog Dam. Throughout the study, dogs were observed swimming in the Hot Dog Dam, and several dog owners related stories of their dogs getting sick after drinking the water in the area. The

isolated input of fecal matter from dogs and animals around the Hot Dog Dam are the cause of the increased levels of E. Coli present at site 12.

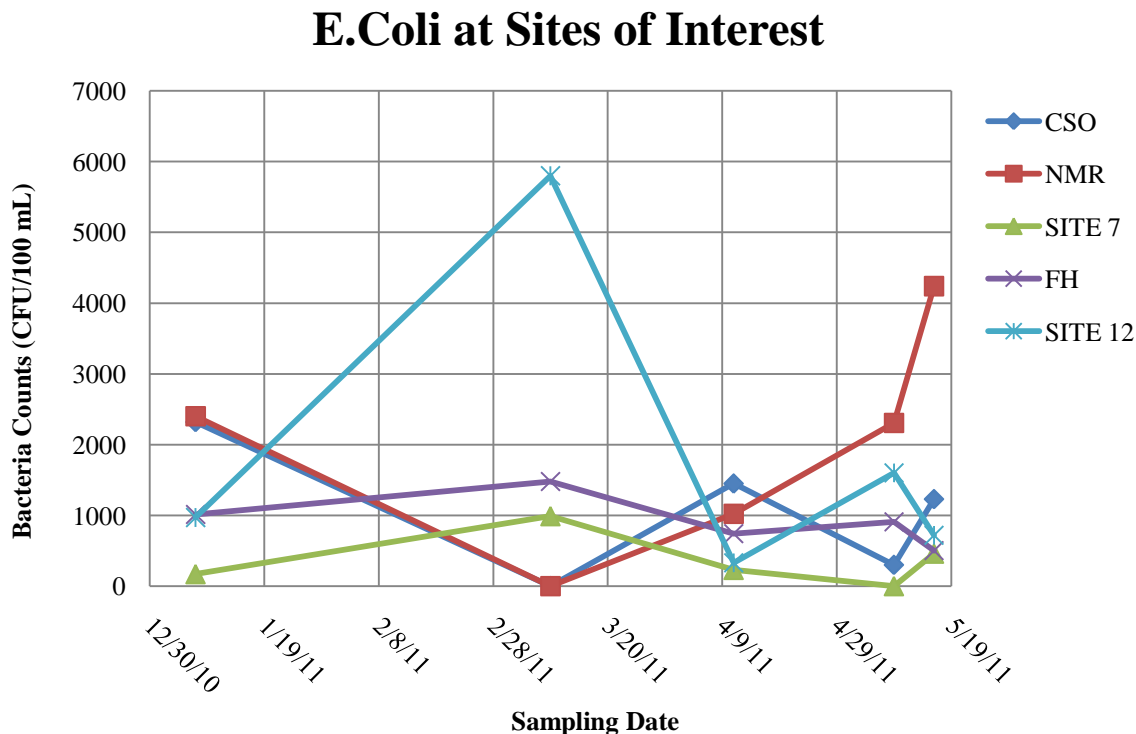


Figure 4-18: E. Coli Plate Counts for 5 Sampling Dates (1/7/11 – 5/16/11) at the CSO site 1, NMR sites, Site 7, Fern Hollow Sites, and Site 12. Site 12 had the single highest count of the sampling period, while NMR averaged the highest.

4.4.3 Turbidity

Turbidity is a measure of the cloudiness of water, and how much suspended material present decreases the passage of light through the water (USEPA, 2010c). Turbidity is also commonly used to evaluate water quality. Suspended materials include soil particles, microbes, and other substances that range in size from 0.004 mm to 1.0 mm (USEPA, 2010c).

High numbers of bacteria have been observed in correlation to waters with high turbidity, which is usually caused by soil erosion, waste discharge, or urban runoff (EPA). This is because

the suspended particles act as a medium for growth (USEPA, 2011a). The impervious surfaces that surround Frick Park provide ideal conditions for rapid increases in stream velocity and erosion rates.

High flow events diluted concentrations of all parameters throughout the study, but bacterial contamination associated with high turbidity was greatest during these high flow events due to increasing wet weather flows from SSOs and CSOs. This is no more apparent than in **Figure 4-19**, which shows stream specific turbidity within the NMR Watershed. The highest turbidity values occurred during the high flow event on 3/10/11 and correspond to the high enterococci counts in **Figure 4-16**. The turbidity values in NMR, FH, and FR during the high precipitation event were 83, 50, and 50 NTU, respectively. During this time, NMR values were 16.5x higher than turbidity averages during the rest of the samplings, while Fern Hollow was 7x higher, and Falls Ravine was 6x higher. Also, during the 5/16/11 sampling, a high precipitation event occurred the day before sampling, which slightly increased turbidity levels, as well as increasing E. Coli and Enterococci counts. With more solids present in the surface water during this time, bacteria had more particles to adsorb to upon entrance to the stream.

Frick Park Stream Turbidity

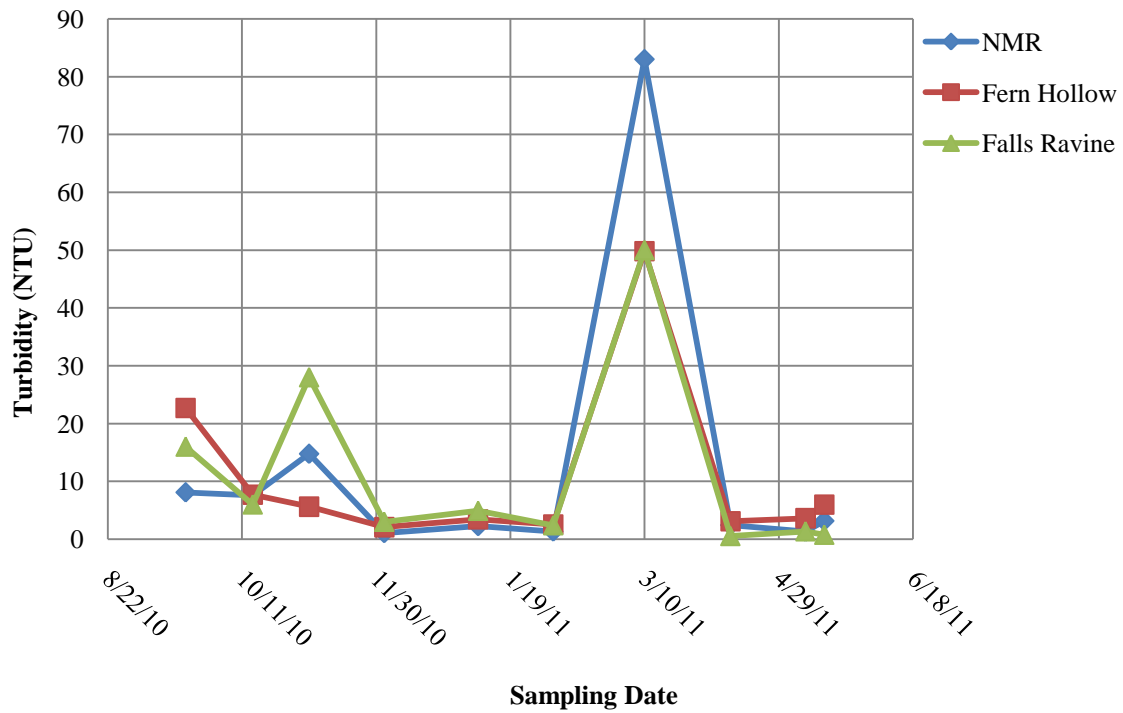


Figure 4-19: Monthly Turbidity (NTU) from 9/20/10 – 5/16/11 for NMR, Fern Hollow, and Falls Ravine. NMR yielded the highest turbidity readings of the study during the high flow event on 3/10/11.

5.0 SUMMARY AND CONCLUSIONS

This study has shown that the water quality in the Nine Mile Run Watershed of Frick Park is adversely affected by influences from deicing agents, fecal contamination from dogs, and contributions from the SSO/CSO systems. Some of these contamination sources are seasonal, like deicing agents, while some contribute year-round contamination like sewage from SSO and CSO systems.

Of the cationic species observed during this study, sodium displayed contamination issues that were a direct result of salt and brine used to deice roadways in the wintertime. NMR averaged the highest sodium values throughout the study with a high of 570 mg/L during the February 2011 sampling. During the months of January and February 2011, 38.2 inches of snow fell resulting in large volumes of deicing agent application. Between this period a 410 mg/L sodium concentration was observed in NMR, while only 210 mg/L was averaged during the remaining months of sampling. This validates the influence of deicing agents to NMR during the winter months.

Calcium displayed influence from both deicing agents and underlying subsurface strata throughout the study, but were not limited to the winter months. Fern Hollow had the highest average calcium concentration of 120 mg/L and a maximum of 270 mg/L. Concentrations were high during the winter months of December – February, as well as the warmer months of April and May showing impact from deicing agents and natural sources. However, magnesium

displayed less influence from deicing agents and more from natural sources. A November 2011 high of 160 mg/L, followed by values in the 90 mg/L range for May 2011, showed independence from deicing contamination during the winter months. The wet, early part of May 2011 could have aided in the release of the mineral from rock and soil at sites along Fern Hollow, resulting in the high magnesium concentrations during this period.

Fern Hollow averaged the highest potassium concentrations of the study with a value of 4.2 mg/L. The CSO site had the highest site concentration of 6.7 mg/L during the 5/16/11 sampling. This could be the result of the heavy usage of fertilizer during this period and the direct input of raw sewage from the CSO.

Anionic concentrations of nitrate (NO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) showed that contamination was present due to deicing agents, fertilizer application in surrounding neighborhoods, and influence from SSO and CSO systems. Chloride concentration proved to be an excellent indicator of deicing agent contamination because of its conservative presence in surface and groundwater. The highest chloride concentrations occurred during January and February of 2011, which corresponded with the same time frame that yielded the highest sodium concentrations. Chloride concentrations as high as 2420 mg/L were recorded during this period at site 5 on NMR. The January values were 2-3.5 times higher than the next highest month of February. Chloride and sodium concentrations were greatest during the winter months, and along NMR because of their use in salt application on I-376, South Braddock Avenue, Commercial Avenue, and other adjacent roadways.

Nitrate was more of a concern due to the potential health affects for downstream drinking water sources. January 2011 yielded the highest average nitrate values of 880 mg/L in NMR, but the charge balance that was conducted for this sampling date, negated these values. A 52% CBE

for this period makes it apparent that some other inorganic/organic source was present during this time, or the sample was inadvertently contaminated. With the exclusion of January, the warmer, higher precipitation months of April and May 2011 had the next highest average concentrations of nitrate (78 mg/L). High nitrate levels during this period would be a result of the combination of increased fertilizer usage in surrounding neighborhoods, and the fertilizer runoff caused large amounts of rainfall. Throughout the study, nitrate concentrations were affected by contributions from fertilizer and CSO/SSO influence. Following a similar trend as that of nitrate in regards to the warmer months; sulfate had the highest concentrations during May 2011. The average sulfate concentrations observed on the 5/9/11 sampling were the only values that exceeded the SMCL of 250 mg/L, concluding that sulfate contamination is negligible.

Bacterial contamination was evaluated by using the indicator organisms Enterococci and E. Coli. Enterococci counts were largest throughout the study at the CSO site (1060 CFU/100 mL) and NMR sites (1050 CFU/100 mL), while site 12 had consistently higher counts than Fern Hollow sites. Site 12 exhibited a 170% increase over the 30 CFU/100 mL for Fern Hollow sites during the 5/9/11 sampling. The single highest E. Coli count of 5800 CFU/100 mL occurred during 3/10/11 at site 12, which corresponds to the highest values of turbidity over the course of the study. Turbidity is a good indicator of bacterial contamination due to the high levels suspended particles. E. Coli counts for site 12 were consistently higher than Fern Hollow sites. However, NMR had the highest average count of 2490 CFU/100 mL throughout the study. Both enterococci and E. Coli results verify that bacterial contamination exists in all Frick Park streams, with Fern Hollow and NMR as the leading contributors. Site-to-site comparisons showed that site 12 is adversely affected by input from pet waste at the “Hot Dog Dam” area.

Also, NMR and the CSO sites received bacterial contamination from sewage inputs from upstream SSO and CSO influence.

All parameters except for the bacteria and turbidity decreased during a high precipitation event that occurred on 3/10/11. It was on this day that the greatest 24-hour precipitation event occurred during March 2011. During this period, 1.23 inches of rain fell, which occurred before, during, and after the sampling. The highly urbanized impermeable surfaces of the neighborhoods surrounding Frick Park encourage fast, high flows during large precipitation events like on 3/10/11. While cationic and anionic compounds were washed-out during this period, the wet weather flows from the CSOs and SSOs caused an increase in the enterococci and E. Coli colony counts.

Of the three Frick Park tributaries studied, NMR produced some of the highest concentrations of the measured parameters, especially with regards to deicing agents (NaCl), and bacteria. Seasonal variations were especially noticed in NMR, with peak concentrations of sodium, chloride, and calcium occurring between December 2010 and February 2011. Spring-fed Falls Ravine consistently yielded concentrations that were well below values observed on Fern Hollow and NMR. Site-to-site comparisons showed that site 12 had higher bacterial concentrations of both E. Coli and Enterococci, when compared to the upstream site 8. Site 5 on NMR, consistently yielded the highest concentrations of all other NMR sites throughout the course of the study. It was also the furthest upstream toward the culverted section of NMR than any other sites. Future studies might want to add additional sites further upstream of site 5 toward the canal-lined section of NMR, and directly beneath the Braddock Avenue outfall.

5.1 RECOMMENDATIONS

Previous research has documented similar issues within NMR (Collins *et al.*, 1998) that has resulted in upgrades in channel design, riparian vegetation, and CSO/SSO awareness, but work done for this thesis indicates that these hazardous conditions still exist. More restorative action should be taken to improve the water quality within Frick Park and mitigate contamination sources listed above. If mitigation is economically unfeasible then the public must be informed of the potential health risks associated with the surface water within Frick Park.

Ensuring driver safety during the winter by application of deicing agents is necessary. Sometimes a reduction of NaCl, brine, or CaCl₂ is not an option, especially during winters with large amounts of snow and ice. Therefore, catchment systems and lined retention ponds are suggested to help reduce the amount of deicing agents that reach NMR. A steep slope exists between NMR and I-376 on the northern side of the highway. Concrete spillways could be installed along the highway to transfer this runoff to catchment basins or retention pond at the base of the slope. The basins would therefore reroute some highway runoff before it reaches NMR and has potential to affect downstream vegetation.

Frick Park has very friendly off-leash rules for certain areas of the park. Quite often, owners abuse these rules and allow their dogs to roam into the surface waters of Frick Park. By doing this, dogs are contributing to bacterial contamination of the tributaries of Frick Park. To mitigate this issue, stiffer penalties should be enforced for pet owners that are caught with their dog off-leash in un-specified areas. This study also showed the magnitude of contamination that results from the “Hot Dog Dam” pet area. Signs should be put up along this area of the park informing park goers that the water contains high levels of bacteria, and exposure can cause

serious health implications. It should also be noted on the signs that the cause of the bacterial contamination is partly due to dog waste.

The CSO, SSO, and storm sewer system in Pittsburgh has been an issue in regards to water quality for decades. It has been demonstrated by data herein that both wet and dry weather flows contribute raw sewage to either culverted or surface water streams in the area. Correcting this problem could require a lengthy timeline and an even larger budget. The sewer infrastructure has to be corrected because it will only get worse with time, and the public health of the Pittsburgh region is affected by it. NMR itself might not change the makeup of the Monongahela River, but a combination of other surface and below ground streams with similar CSO and SSO inputs could greatly affect a main drinking water source for the City of Pittsburgh and regions downstream.

BIBLIOGRAPHY

Acumedia., 2011, M-TEC AGAR 7421, Rev 2.
http://www.neogen.com/Acumedia/pdf/ProdInfo/7421_PI.pdf , accessed June 6, 2011.

Anibas, Christian, Kerst Buis, Ronny Verhoeven, Patrick Meire, and Okke Batelaan., 2011, A Simple Thermal Mapping Method for Seasonal Spatial Patterns of Groundwater–Surface Water Interaction. *Journal of Hydrology*, 397, pp: 93-104.

AWWA, APHA, WEF., 1992, *Standard Method for the Examination of Water and Wastewater Methods 3110 and 3111 A,B*. 18th Edition.

AWWA, APHA, WEF., 1998a, *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Section 9222.

AWWA, APHA, WEF., 1998b, *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Section 9215.

Backstrom, M., Karlsson, S., Backman, L., Folkesson, L., Lind, B., 2004, Mobilisation of Heavy Metals by Deicing Salts in a Roadside Environment. *Water Research*, 38(3), pp: 720-732.

Bruce, B., McMahon, P., 1996, Shallow Ground-water Quality beneath a Major Urban Center: Denver, Colorado USA. *Journal of Hydrology*, 186.1(4), pp: 129-51.

CDC., 2010, Salmonella Infection (salmonellosis) and Animals. Centers for Disease Control and Prevention. <http://www.cdc.gov/healthypets/diseases/salmonellosis.htm> , accessed June 12, 2011.

Collins, T., Dzombak, D., Rawlins, J., Tamminga, K., Thompson, S., 1998, Nine Mile Run Watershed Rivers Conservation Plan. Report, *in cooperation with* The City of Pittsburgh, Commonwealth of Pennsylvania Department of Conservation and Natural Resources, and Rivers Conservation Plan.

DEQ, 2010, About Beach Monitoring in Michigan. Department of Environmental Quality. http://www.michigan.gov/deq/0,1607,7-135-3313_3686_3730-11005--,00.html , accessed June 15, 2011.

Difco. m-Enterococcus Agar, *The Difco Manual*, Section II, pp: 187-188.

Dionex., 2004, Determination of Inorganic Anions in Drinking Water by Ion Chromatography. Report Vol. 133, *in coordination with* Dionex (California).

El Samrani, A.G., Lartiges, B.S., Villieras F., 2008, Chemical Coagulation of Combined Sewer Overflows: Heavy Metal Removal and Treatment Optimization. *Water Research*, 42(4-5), pp: 951-950.

Fetter, C.W., 2001, Applied Hydrogeology – 4th Edition. By *Prentice-Hall, Inc., Upper Saddle River, New Jersey*, pp: 373-374.

Fisher Scientific., 2007, Accumet Chloride Combination Ion Selective Electrodes. *Instructions for Catalog No. 13-620-627 by Fisher Scientific.*

Fleckenstein, J.H., Krause, S., Hannah, D.M., Boano, F., 2010, Groundwater-surface Water Interactions: New Methods and Models to Improve Understanding of Processes and Dynamics. *Advances in Water Resources*, 33, pp:1291-1295.

Galloway, J.N., Townsend, A.R., Erismann, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008, Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. *Science*, 320, pp: 889-892.

Gromaire, M. C., Garnaud, S., Saad, M., Chebbo, G., 2001, Contribution of Different Sources to the Pollution of Wet Weather Flows in Combined Sewers. *Water Research*, 35(2), pp:521-533.

Kazezyilmazalhan, C., Medinajr, M., 2006, Stream Solute Transport Incorporating Hyporheic Zone Processes. *Journal of Hydrology*, 329(1-2), pp: 26-38.

Kelly, W.R., Panno, S.V., Hackley, K.C., Hwang, H., Martinsek, A.T., Markus, M., 2010, Using chloride and other ions to trace sewage and road salt in the Illinois Waterway. *Applied Geochemistry*, 25, pp: 661-673.

Koryak, M., Stafford, L.J., Rosemary, J.R., Magnuson, P.M., 2001a, Highway Deicing Salt Runoff Events and Major Ion Concentrations along a Small Urban Stream. *Journal of Freshwater Ecology*, 16(1), pp: 125-134.

Koryak, M., Hoskin, R.H., Reilly, R.J., Stafford, L.J., 2001b, The Impact of Above Grade Sewerline Crossings on the Distribution and Abundance of Fishes in Recovering Small Urban Streams of the Upper Ohio River Valley. *Journal of Freshwater Ecology*, 16(4), pp: 591-598.

Krause, S., Bronstert, A., Zehe, E., 2007, Groundwater-surface water interactions in a North German lowland floodplain – Implications for the river discharge dynamics and riparian water balance. *Journal of Hydrology* 347(3-4), pp: 404-417.

Lacour, C., Joannis, C., Chebbo, G., 2009, Assessment of Annual Pollutant Loads in Combined Sewers from Continuous Turbidity Measurements: Sensitivity to Calibration Data. *Water Research*, 43(8), pp: 2179-2190.

Lenntech, 1998-2009, Potassium (K) and Water Treatment and Purification - Lenntech. Report, *in cooperation with Lenntech Water Treatment & Purification Holding B.V.* <http://www.lenntech.com/periodic/water/potassium/potassium-and-water.htm>, accessed April 26, 2011.

Lerner, D.N., Harris, B., 2009, The Relationship between Land Use and Groundwater Resources and Quality. *Land Use Policy*.

Meays, C., K. Broersma, R. Nordin, and A. Mazumder., 2004, Source Tracking Fecal Bacteria in Water: a Critical Review of Current Methods. *Journal of Environmental Management*, 73(1), pp: 71-79.

Munck, I., Bennett, A., Chandalin, M., Camilli, K.S., Nowak, R.S., 2010, Long-term impact of de-icing salts on tree health in the Lake Tahoe Basin: Environmental influences and interactions with insects and diseases. *Forest Ecology and Management*, 260, pp: 1218-1229.

Nine Mile Run Watershed Association, 2011, Nine Mile Run Watershed Monitoring, Water Quality Reports. <http://www.ninemilerun.org/nine-mile-run-watershed-monitoring/>, accessed March 14, 2011.

NOAA, 2011, National Weather Service Forecast Office – Monthly Weather Summary for Pittsburgh, PA. <http://www.weather.gov/climate/index.php?wfo=pbz> , accessed June 17, 2011.

Ostendorf, D.W., Hinlein, E.S., Rotaru, C., DeGroot, D.J., 2006, Contamination of groundwater by outdoor highway deicing agent storage. *Journal of Hydrology*, 326, pp: 109-121.

PennDOT, 2010a, Winter Maintenance Notes. Report, *in cooperation with Pennsylvania Department of Transportation* (PennDOT District 6-0). http://www.dot.state.pa.us/pennDOT/districts/district6.nsf/winter_maint_notes?ReadForm , accessed March 3, 2011.

PennDOT, 2010b, Winter Services Guide 2010-2011 - Winter Facts. Report, *in cooperation with Pennsylvania Department of Transportation*.

Perkin Elmer Co., 1988, Flame Atomic Absorption Spectrophotometric –Principle and Instrumentation - Model 1100B Atomic Absorption Spectrophotometer Operator's Manual. *Publication B398, by the Perkin Elmer Co. GmbH, D-7770*.

Savichtcheva, O., and S. Okabe., 2006, Alternative Indicators of Fecal Pollution: Relations with Pathogens and Conventional Indicators, Current Methodologies for Direct Pathogen Monitoring and Future Application Perspectives. *Water Research*, 40(13), pp: 2463-2476.

Slanetz, L. W. and Bartley, C. H., 1957, Numbers of enterococci in water, sewage, and faeces determined by the membrane filter technique with an improved medium. *J. Bact.*, 74, pp: 591-595.

Venner Consulting and Parsons Brinckerhoff, 2004, Environmental Stewardship Practices, Procedures, and Policies for Highway Construction and Maintenance - Chapter 8. Report, *in cooperation with* American Association of State Highway and Transportation Officials (AASHTO).

Weyrauch, P., Matzinger, A., Pawlowsky-Reusing, E., Plume, S., Von Seggern, D., Heinzmann, B., Schroeder, K., Rouault, P., 2010, Contribution of Combined Sewer Overflows to Trace Contaminant Loads in Urban Streams. *Water Research*, 44, pp: 4451-4462.

Williams, D. D., Williams, N.E., Cao, Y., 1999, Road Salt Contamination of Groundwater in a Major Metropolitan Area and Development of a Biological Index to Monitor Its Impact. *Water Resources*, 34(1), pp: 127-138.

USEPA, 2011b, Water, Watershed, Environmental Information, Related Information of Region 3, Combined Sewer Overflows (CSOs) and Sanitary Sewer Overflows (SSOs). http://water.epa.gov/type/location/regions/region3_index.cfm , accessed March 13, 2011.

USEPA., 1997, EPA Method 1600: Membrane Filter Test Method for Enterococci in Water, EPA- 821-R-97-004, Method, *in coordination with* US Environmental Protection Agency, Office of Water.

USEPA., 2010a, Basic Information about Nitrate in Drinking Water. United States Environmental Protection Agency. <http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm> , accessed June 10, 2011.

USEPA., 2010b, Sulfate in Drinking Water. United States Environmental Protection Agency. <http://water.epa.gov/drink/contaminants/unregulated/sulfate.cfm>, accessed June 10, 2011.

USEPA., 2010c, Water: Monitoring and Assessment – 5.5 Turbidity. United States Environmental Protection Agency. <http://water.epa.gov/type/rsl/monitoring/vms55.cfm>, accessed June 7, 2011.

USEPA., 2011a, Basic Information about Pathogens and Indicators in Drinking Water. Water: Information about Regulated Drinking Water Contaminants by the United States Environmental Protection Agency. <http://water.epa.gov/drink/contaminants/basicinformation/pathogens.cfm> , accessed June 7, 2011.

USGS., 2011, USGS 03085000 Monongahela River at Braddock, PA Water Quality Data - National Water Information System: Web. The US Geological Survey. Interface, http://nwis.waterdata.usgs.gov/nwis/qwdata/?site_no=03085000&agency_cd=USGS&format=inventory&inventory_output=retrieval&rdb_inventory_output=file&TZoutput=0&pm_cd_compare=Greater_than&radio_parm_cds=all_parm_cds&qw_attributes=0&qw_sample_wide=wide&rdb_q , accessed May 29, 2011.